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HEAT-DEVELOPABLE COLOR PHOTOGRAPHIC LIGHT-SENSITIVE MATERIAL
[NETSUGENZO KARAA KANKO ZAIRYO]

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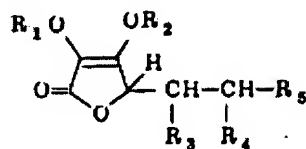
Specification

1. Title of the Invention: Heat-developable color photographic light-sensitive material

2. What is Claimed is:

A heat-developable color photographic light-sensitive material which has at least a light-sensitive silver halide, a binder, a non-diffusible dye-providing compound which releases a diffusible dye on being reduced, an electron donor and an electron transferring agent on a substrate, characterized in that it further contains a compound represented by the following formula [I]:

General Formula [I]



wherein R_1 and R_2 each represents a hydrogen atom or a substituted or unsubstituted alkyl group, aryl group, acryl group or alkoxycarbonyl group; and R_3 to R_5 each represents a hydrogen atom, a hydroxyl group, a halogen atom, a nitro group, a sulfo group, a cyano group or a substituted or unsubstituted alkyl group, aryl group, alkoxy group, aryloxy group, acyl group, acyloxy group, carbonate group or amino group.

Further, in the case where R_1 or R_2 represents a hydrogen atom, a salt can be formed with a monovalent to trivalent metal ion while either or both hydroxyl groups are being released.

3. Detailed Description of the Invention

<Industrial Applicability>

The present invention relates to a heat-developable color photographic light-sensitive material and, in particular, to a heat-developable color photographic light-sensitive material capable of providing positive color images having a high image density and fewer stains.

<Background of the Invention>

Heat-developable light-sensitive materials are known in the art and heat-developable light-sensitive materials and processes for processing them are described, for example, in "Shashin Kogaku no Kiso" (Tr. "The Basis of Photographic Engineering"), Non-Silver Salt Photography, pages 242 to 255, published by Corona Sha, (1982) and U.S. Patent No. 4500626.

Various processes for obtaining positive color images by heat development have also been proposed.

/2

For example, U.S. Patent No. 4559290 proposes a process wherein a compound obtained by converting a so-called DRR compound to an oxidation-type compound having no dye-releasing ability is allowed to coexist with a reducing agent, the

reducing agent is oxidized by heat development according to an exposure of the silver halide, and a diffusible dye is released by the reduction with the remaining reducing agent without being oxidized. Further, European Patent Publication No. 220746 and Published Technical Report 87-6199 (Published Technical Report Vol. 12, No. 22) describe a heat developable positive image forming method which uses a novel compound which releases a diffusible dye in the same mechanism as above.

However, it was found that the above-described heat developable color photographic light-sensitive materials which are capable of providing positive color images were not in the level of commercially available coupler print materials from the standpoint of stains, image sharpness and tone reproducibility.

<Problem to be Solved by the Invention>

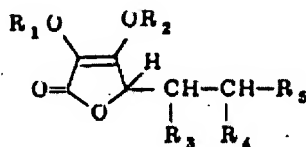
The object of the present invention is to improve the S/N ratio, image sharpness and tone reproducibility of a heat-developable color photographic light-sensitive material using a reducible dye-providing compound.

<Means of Solving the Problem>

The object of the present invention was achieved by a heat-developable color photographic light-sensitive material which had at least a light-sensitive silver halide, a binder, a non-diffusible dye-providing compound which released a diffusible dye on being reduced ("reducible dye-providing compound",

hereinafter), an electron donor and an electron transferring agent on a substrate, characterized in that it further contained a compound represented by the following formula [I]:

General Formula [I]



wherein R_1 and R_2 each represents a hydrogen atom or a substituted or unsubstituted alkyl group, aryl group, acryl group or alkoxycarbonyl group; and R_3 to R_5 each represents a hydrogen atom, a hydroxyl group, a halogen atom, a nitro group, a sulfo group, a cyano group or a substituted or unsubstituted alkyl group, aryl group, alkoxy group, aryloxy group, acyl group, acyloxy group, carbonate group or amino group.

Further, in the case where R_1 or R_2 represents a hydrogen atom, a salt can be formed with a monovalent to trivalent metal ion while either or both hydroxyl groups are being released.

Examples of compounds that can be represented by the above formula [I] include L-ascorbic acid derivatives, which are known as vitamin C, and D-isoascorbic acid derivatives.

In the field of light-sensitive materials, ascorbic acid derivatives are conventional materials, which are used as developing main agents and have a structure satisfying the Kendall-Peltz rule. The compounds represented by general formula

[I] according to the present invention are described in greater detail below.

In general formula [I], R_1 and R_2 each represents a hydrogen atom or a substituted or unsubstituted alkyl group (e.g., methyl, ethyl, hydroxyethyl, butyl and cyclohexyl having 20 or less carbon atoms), aryl group (e.g., phenyl and sulfophenyl having 20 or less carbon atoms), acryl group (e.g., acetyl and benzoyl having 20 or less carbon atoms) or alkoxycarbonyl group (e.g., methoxycarbonyl and phenoxycarbonyl having 20 or less carbon atoms).

The compound represented by general formula [I] is preferably water-soluble on developing. Therefore, R_1 and R_2 is each preferably a hydrogen atom, a metal salt which can be released on processing, or a group which can be readily hydrolyzed on processing.

R_3 to R_5 each preferably represents a hydrogen atom, a hydroxyl group, a halogen atom (e.g., fluorine, chlorine and bromine), a nitro group, a sulfo group, a cyano group or a substituted or unsubstituted alkyl group (preferably having 20 or less carbon atoms, such as methyl, ethyl, propyl, pentadecyl, cyclohexyl and hydroxyethyl), aryl group (preferably having 20 or less carbon atoms, such as phenyl and tolyl), alkoxy group (preferably having 20 or less carbon atoms, such as methoxy, ethoxy, and methoxy ethoxy), aryloxy group (preferably having 20

or less carbon atoms, such as phenoxy), acyl group (preferably having 20 or less carbon atoms, such as acetyl and benzoyl), acyloxy group (preferably having 20 or less carbon atoms,

/3

such as acetyloxy, propionyloxy, heptanoyloxy, palmitoyloxy and benzoyloxy), carbonate group (preferably having 20 or less carbon atoms, such as methoxycarbonyl, ethoxycarbonyl and phenoxycarbonyl), or amino group (preferably having 20 or less carbon atoms, such as -NH_2 , dimethylamino, N,N-di-hydroxyethylamino). Of these, from the standpoint of the water-solubility, the carbon number is particularly preferably 4 or less.

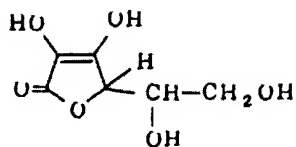
Further, two or more of R_3 to R_5 can be taken together to form a ring.

The proportion of the compound represented by general formula [I] is 1/20 to 5 times (mol) the proportion of an electron transferring agent (ETA), and is more preferably 1/10 to 2 times (mol).

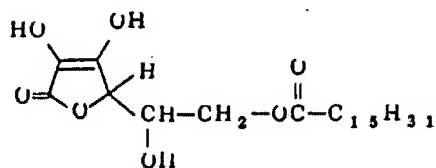
The layer to which the compound represented by general formula [I] is added is not particularly restricted but can be added to any of a light-sensitive layer, an intermediate layer, a protective layer and a subbing layer, with the addition to the intermediate layer being more effective.

Specific examples of compounds represented by general formula [I] are as follows:

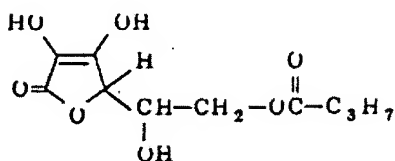
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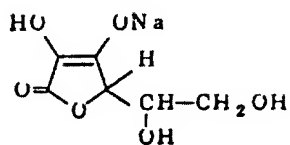
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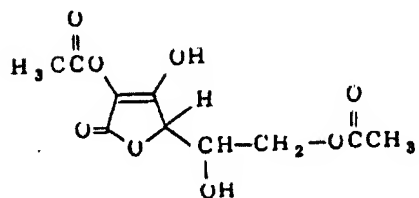
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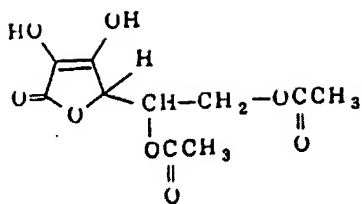
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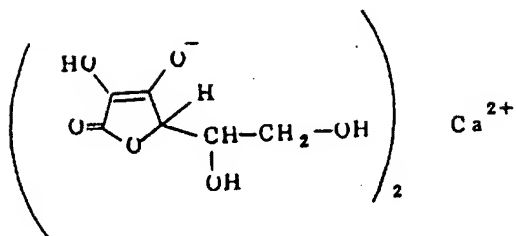
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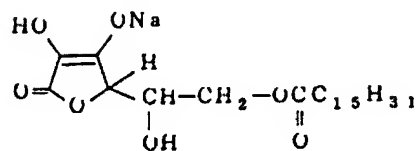
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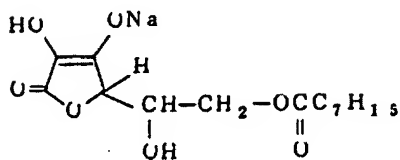
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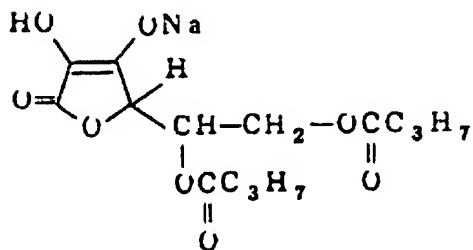
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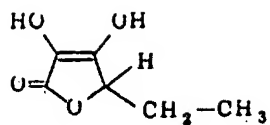
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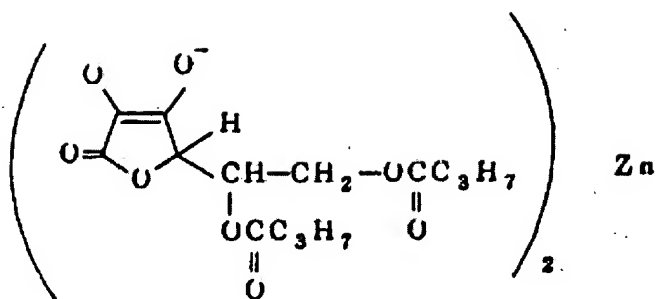


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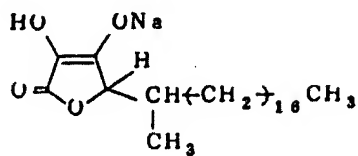


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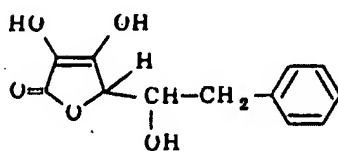
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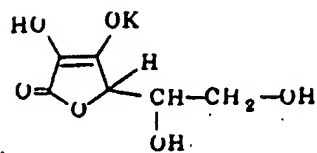
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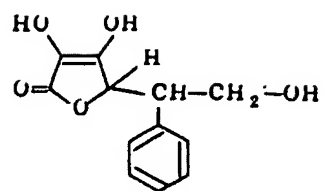
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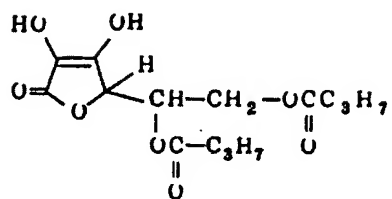
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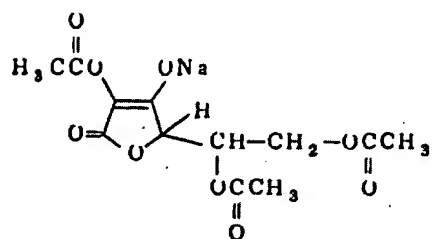
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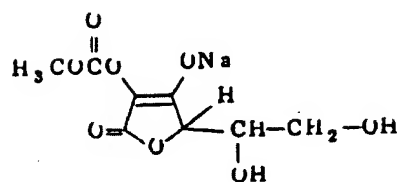
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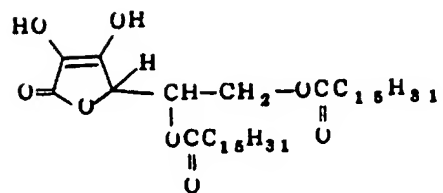
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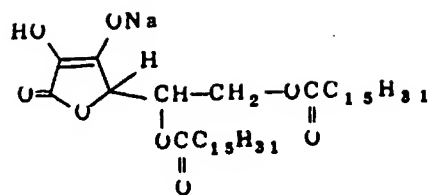
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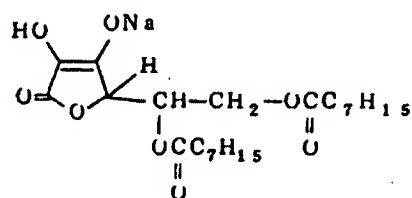
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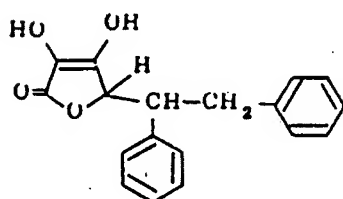
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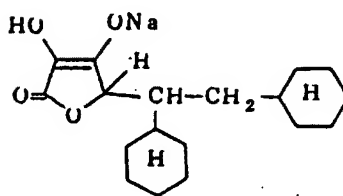
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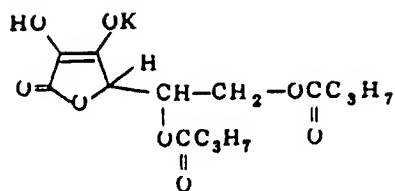


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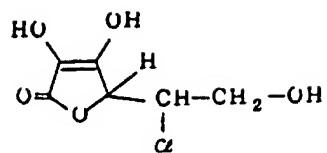


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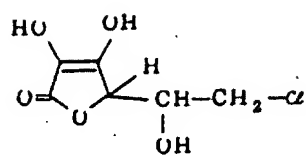
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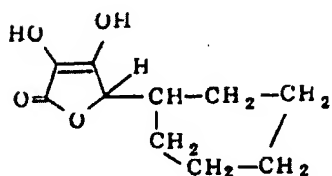
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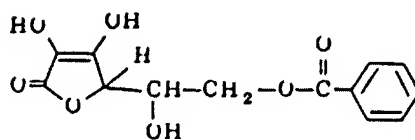
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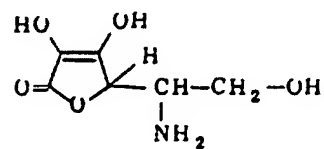
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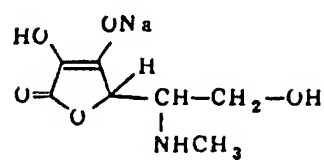
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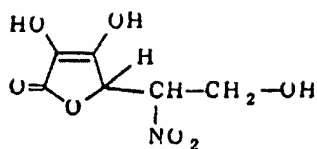
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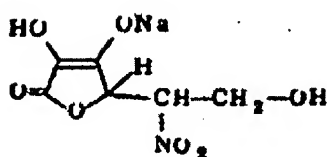
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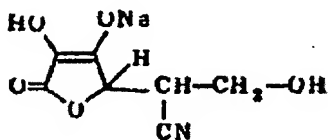
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AS-33



AS-34



In the present invention, one unit of light-sensitive layer is obtained by a combination of a reducible dye-providing compound, together with an electron transferring agent and an electron donor, with a binder and a silver halide emulsion. The reducible dye-providing compound can be added to the same layer as the layer to which the silver halide emulsion is added, but they also can be separately added to adjacent layers. In the latter case, the reducible dye-providing compound layer is preferably located under the silver halide emulsion layer from the standpoint of the sensitivity. In this case, the electron

transferring agent and the electron donor can be added to any of the silver halide emulsion layer and the reducible dye-providing compound layer,

/6

it is preferred that the electron transferring agent is present in the silver halide emulsion layer. In the present invention, at least two sets of such light-sensitive layers are used. In order to reproduce full colors, three sets of light-sensitive layers each having a different color sensitivity are generally used. Known examples of the combination include a 3 layer combination of a blue-sensitive layer, a green-sensitive layer and a red-sensitive layer, and a 3 layer combination of a green-sensitive layer, a red-sensitive layer and an infrared-sensitive layer. These light-sensitive layers can be disposed in various disposition orders as known from conventional color photographic light-sensitive materials. In addition, as needed, each light-sensitive layer can also be composed of two or more layers.

Next, the reducible dye-providing compounds that can be used in the present invention are described in the following.

The reducible dye-providing compound used in the present invention is preferably a compound represented by the following formula (C-I):

PWR-(Time)_t-Dye General Formula (C-I)

wherein PWR represents a group which releases $-(\text{Time})_t\text{-Dye}$ by being reduced.

Time represents a group which releases Dye through a subsequent reaction after being released from PWR as $-(\text{Time})_t\text{-Dye}$.

t represents an integer of 0 to 1.

Dye represents a dye or a precursor thereof.

First, PWR is described in greater detail.

PWR can be a group corresponding to a moiety containing the electron acceptive center and the intramolecular nucleophilic substitution reaction center in a compound capable of releasing a photographic reagent by an intramolecular nucleophilic substitution reaction after being reduced as disclosed in U.S. Patent. No. 4,139,389, U.S. Patent. No. 4,139,379 and U.S. Patent. No. 4,564,577, Japanese Unexamined Patent Publication No. S59-185333 and Japanese Unexamined Patent Publication No. S57-84453, or can be a group corresponding to a moiety containing the electron acceptive quinoid center and the carbon atom bonding the quinoid center to a photographic reagent in a compound capable of releasing the photographic reagent by an intramolecular electron transfer reaction after being reduced as disclosed in U.S. Patent No. 4,232,107, Japanese Unexamined Patent Publication No. S59-101649, Research Disclosure (1984) IV, 24025, and Japanese Unexamined Patent Publication No. S61-88257. Further, PWR can be a group corresponding to a moiety containing

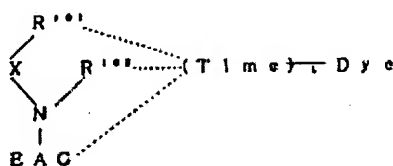
the aryl group substituted by an electron attractive group and the atom (a sulfur atom, a carbon atom, or a nitrogen atom) bonding the aryl group to a photographic reagent in a compound capable of releasing the photographic reagent by the cleavage of a single bond after being reduced as disclosed in Japanese Unexamined Patent Publication No. S56-142530, U.S. Patent No. 4,343,893 and U.S. Patent No. 4,619,884. Further, it can be a group corresponding to a moiety containing the nitro group and the carbon atom bonding the nitro group to a photographic reagent in a nitro compound capable of releasing the photographic reagent after receiving electrons as disclosed in U.S. Patent. No. 4,450,223, or can also be a group corresponding to a moiety containing the geminaldinitro moiety and the carbon atom bonding the geminaldinitro moiety to a photographic reagent in a dinitro compound capable of releasing the photographic reagent by a β -elimination reaction after receiving electrons as disclosed in U.S. Patent. No. 4,609,610.

Further, examples of compounds as PWR include: a compound having a $\text{SO}_2\text{-X}$ (wherein X represents an oxygen atom, a sulfur atom or a nitrogen atom) and an electron attractive group in the molecule as disclosed in Japanese Patent Application No. S62-106885; a compound having a PO-X bond (wherein X is the same as above) and an electron attractive group in the molecule as disclosed in Japanese Patent Application No. S62-106895; and a

compound having a C-X' bond (wherein X' is the same as X or represents -SO₂-) and an electron attractive group in the molecule as disclosed in Japanese Patent Application No. S62-106887.

In order to more sufficiently achieve the object of the present invention, of the compounds represented by general formula [C-I], those which can be represented by general formula [C-II] are preferred.

General Formula [C-II]



(Time)_tDye is bonded to at least one of R¹⁰¹, R¹⁰², and EAG.

The moiety corresponding to PWR of general formula [C-II] is described.

X represents an oxygen atom (-O-), a sulfur atom (-S-) or a nitrogen-containing group (-N(R¹⁰³)-).

R¹⁰¹, R¹⁰², and R¹⁰³ each represent a group besides a hydrogen atom or a simple bond.

/7

Examples of the groups besides a hydrogen atom represented by R¹⁰¹, R¹⁰², and R¹⁰³ include an alkyl group, an aralkyl group, an alkenyl group, an alkynyl group, an aryl group, a

heterocyclic group, a sulfonyl group, a carbamoyl group and a sulfamoyl group, and these groups can have a substituent.

R^{101} and R^{103} each preferably represents an alkyl group, an alkenyl group, an alkynyl group, an aryl group, a heterocyclic group, an acyl group or a sulfonyl group, each of which can be substituted or unsubstituted. The carbon number of each group represented by R^{101} and R^{103} is preferably 1 to 40.

R^{102} preferably represents a substituted or unsubstituted acyl group or sulfonyl group. Examples of the acyl group and sulfonyl group include the same as described in R^{101} and R^{103} . The carbon number is preferably 1 to 40.

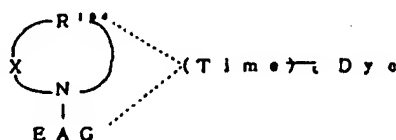
R^{101} , R^{102} and R^{103} may be combined with each other to form a 5- to 8-membered ring.

X is particularly preferably an enzyme.

EAG will be described later.

In order to achieve the object of the present invention, of the compounds represented by general formula [C-II], compounds represented by general formula [C-III] are preferred:

General Formula [C-III]



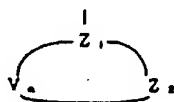
(Time)₂Dye is bonded to at least either R^{104} or EAG.

X is the same as described above.

R^{104} represents an atomic group forming a 5- to 8-membered monocyclic or condensed heterocyclic ring containing the nitrogen atom by combining with X and the nitrogen atom.

EAG represents a group capable of accepting an electron from a reducing substance and is bonded to the nitrogen atom. EAG is preferably a group represented by the following general formula [A]:

General Formula [A]

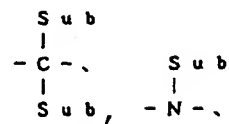


In general formula [A],

Z_1 represents $\begin{array}{c} | \\ -C- \\ | \end{array} \text{Sub}$ or $\begin{array}{c} | \\ -N- \end{array}$.

V_n represents an atomic group forming a 3- to 8-membered aromatic group with Z_1 and Z_2 , and n represents an integer of 3 to 8.

V_3 represents $-Z_3-$, V_4 represents $-Z_3-Z_4-$, V_5 represents $-Z_3-Z_4-Z_5-$, V_6 represents $-Z_3-Z_4-Z_5-Z_6-$, V_7 represents $-Z_3-Z_4-Z_5-Z_6-Z_7-$, and V_8 represents $-Z_3-Z_4-Z_5-Z_6-Z_7-Z_8-$.



In the above formulae, Z_2 to Z_8 each represents $\begin{array}{c} \text{Sub} \\ | \\ -C- \\ | \\ \text{Sub} \end{array}$, $-O-$, $-S-$ or $-SO_2-$, and Sub represents a simple bond (π -bond), a hydrogen atom or the substituent shown below. The Subs can be the same or different, and may combine with each other to form a

3- to 8-membered saturated or unsaturated carbon ring or heterocyclic ring.

In general formula [A], Subs are selected such that the total sum of the Hammett's substituent constants σ -para of the substituents is preferably +0.50 or more, is more preferably +0.70 or more, and is most preferably +0.85 or more.

The EAG is preferably an aryl group or heterocyclic group substituted by at least one electron attractive group. The substituents bonded to the aryl group or the heterocyclic group of EAG can be used for controlling the properties of the whole compound. Examples of the properties of the whole compound include the acceptability of electrons as well as the water-solubility, the oil-solubility, the diffusibility, the sublimability, the melting point, the dispersibility for a binder such as gelatin or the like, the reactivity for a nucleophilic group and the reactivity for an electrophilic group.

/8

Specific examples of EAG are described in European Patent No. 220746A2, pages 6 to 7.

Time represents a group capable of releasing Dye via the subsequent reaction by the cleavage of a nitrogen-oxygen bond, a nitrogen-nitrogen bond or a nitrogen-sulfur bond as a trigger.

Various groups that can be represented by Time are known; known examples of such groups include those described in

Japanese Unexamined Patent Publication No. S61-147244, pages 5 and 6, Japanese Unexamined Patent Publication No. S61-236549, pages 8 to 14, and Japanese Patent Application No. S61-88625, pages 36 to 44.

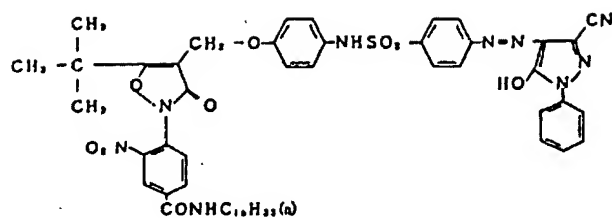
Known examples of the dyes represented by Dye include azo dyes, azomethine dyes, anthraquinone dyes, naphthoquinone dyes, styryl dyes, nitro dyes, quinoline dyes, carbonyl dyes and phthalocyanine dyes. Further, these dyes can be used in the form of being temporarily shifted to a shorter wavelength side, which can be recolored on development.

Specific examples of the Dyes include those disclosed in European Patent No. 76,492A and Japanese Unexamined Patent Publication No. S59-165054.

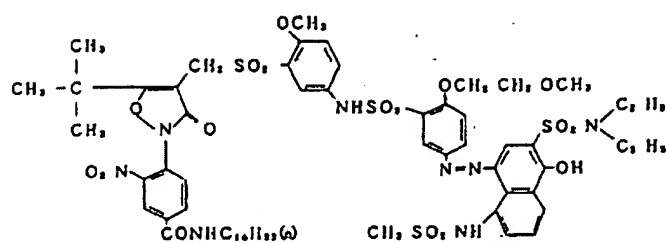
It is necessary that the compound represented by the above general formula [C-II] or [C III] is immobile in a photographic layer; therefore, it is preferred that the compound has a ballast group having 8 or more carbon atoms at the position of EAG, R^{101} , R^{102} , R^{104} or X (in particular, at the position of EAG).

Typical examples of the reducible dye-providing compound used in the present invention are specifically listed below, but these examples do not restrict the present invention in any way but the reducible dye-providing compound described, for example, in European Patent No. 220746A2 and Published Technical Report No. 87-6199 can also be used in the present invention.

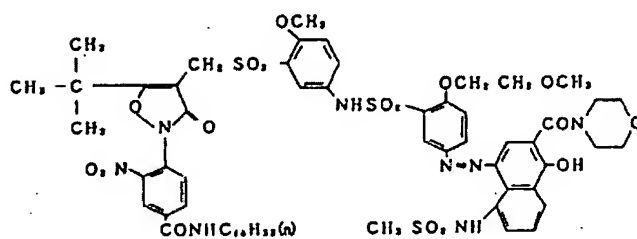
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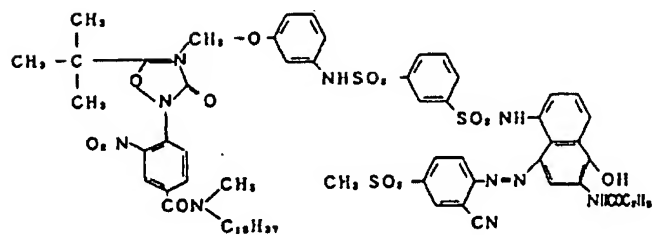
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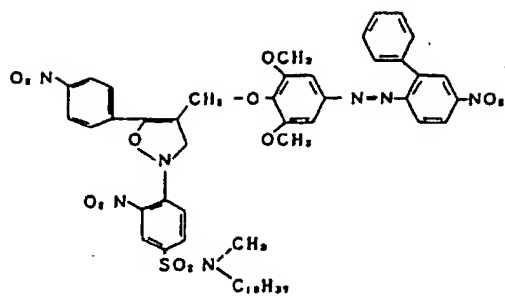
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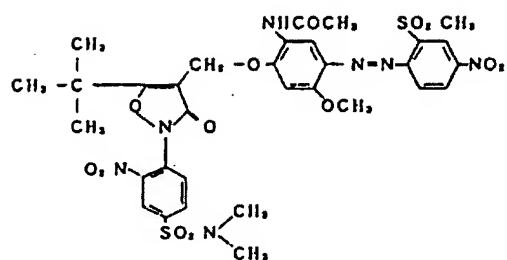
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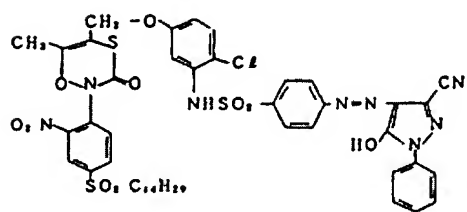
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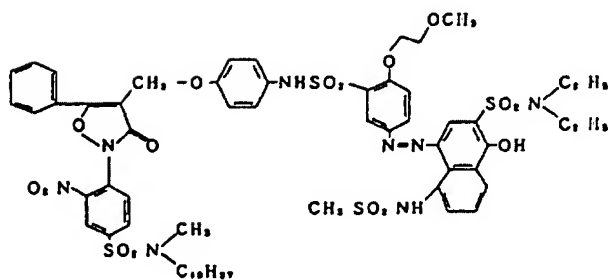
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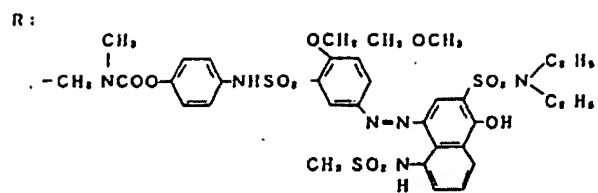


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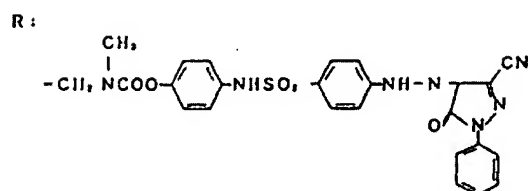
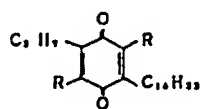


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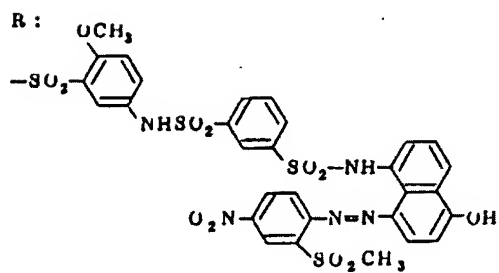
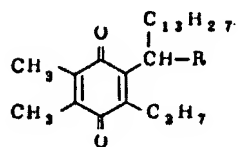




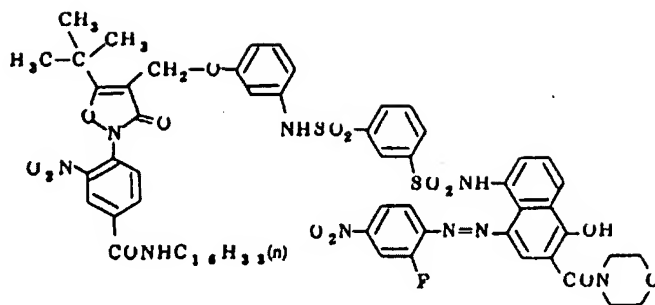
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(16)



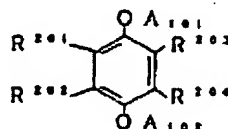
These compounds can be synthesized by the methods described in the above-mentioned patent specifications.

The amount of the dye-providing compound may vary depending on the extinction coefficient of the dye, but is usually in a range of from 0.05 to 5 mmol/m², and is preferably in a range of from 0.1 to 3 mmol/m². The dye-providing compounds can be used alone or in combination of two or more. Further, in order to obtain black images or images composed of different colors, two or more types of dye-providing compounds each releasing a mobile dye each having a different color can be used as a mixture thereof in such a way that a mixture of, for example, at least one type of a cyan dye-providing compound, at least one type of a magenta dye-providing compound and at least one type of a yellow dye-providing compound is incorporated into a layer containing silver halide or a layer adjacent to the silver halide-containing layer as described in Japanese Unexamined Patent Publication No. S60-162251.

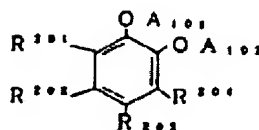
In the present invention, an electron donor and an electron transferring agent (ETA) are used, the details of which are

described in European Patent No. 220746A2 and Published Technical Report 87-6199. Particularly preferred electron donors (and the precursors thereof) are the compounds represented by following general formula [C] or [D]:

General Formula [C]



General Formula [D]



wherein A_{101} and A_{102} each represents a hydrogen atom or a protective group for a phenolic hydroxyl group, said protective group being releasable by a nucleophilic reagent.

In this case, examples of the nucleophilic reagent include anionic reagents, such as $OH^{(-)}$, $RO^{(-)}$ (wherein R represents an alkyl group, an aryl group or the like) and hydroxamic acid anions $SO_3^{2(-)}$, and compounds having a non-covalent electron pair, such as primary or secondary amines, hydrazines, hydroxylamines, alcohols and thiols.

Preferred examples of A_{101} and A_{102} include a hydrogen atom, an acyl group, an alkylsulfonyl group, an arylsulfonyl group,

/11

an alkoxy carbonyl group, an aryloxy carbonyl group, a dialkylphosphoryl group, a diarylphosphoryl group, and the protective groups disclosed in Japanese Unexamined Patent Publication No. S59-197037 and Japanese Unexamined Patent Publication No. S59-20105 and, if possible, A_{101} and A_{102} may combine with R^{201} , R^{202} , R^{203} and R^{204} to form a ring. In addition, A_{101} and A_{102} can be the same or different from each other.

R^{201} , R^{202} , R^{203} and R^{204} each represents a hydrogen atom, an alkyl group, an aryl group, an alkylthio group, an arylthio group, a sulfonyl group, a sulfo group, a halogen atom, a cyano group, a carbamoyl group, a sulfamoyl group, an amido group, an imido group, a carboxyl group, a sulfonamido group or the like. These groups can, if possible, have a substituent.

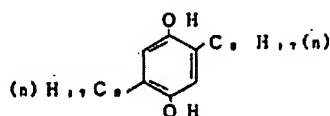
In addition, the sum of the carbon atoms of the groups represented by R^{201} , R^{202} , R^{203} and R^{204} is 8 or more. Further, in general formula [C], R^{201} and R^{202} and/or R^{203} and R^{204} may combine with each other to form a saturated or unsaturated ring, and in general formula [D], R^{201} and R^{202} , R^{202} and R^{203} , and/or R^{203} and R^{204} may combine with each other to form a saturated or unsaturated ring.

In the electron donors represented by the above general formula [C] or [D], it is preferred that at least two of R^{201} to R^{204} are substituents besides a hydrogen atom. Compounds in which

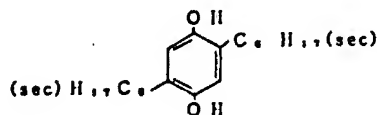
at least one of R^{201} and R^{202} and at least one of R^{203} and R^{204} are substituents besides hydrogen atom are particularly preferred.

The electron donors can be used in a combination thereof, and the electron donor can also be used together with the precursor thereof. Further, the electron donor can be the same compound as the reducing substances used in the present invention. Specific examples of the electron donor are listed below, but this is not an exhaustive list.

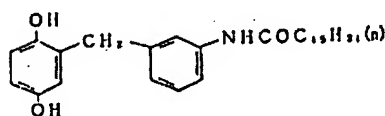
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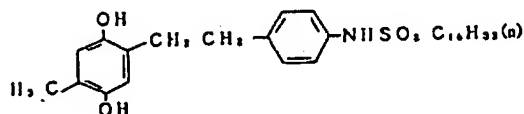
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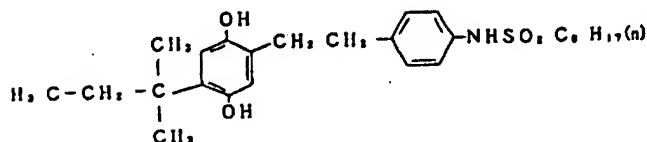
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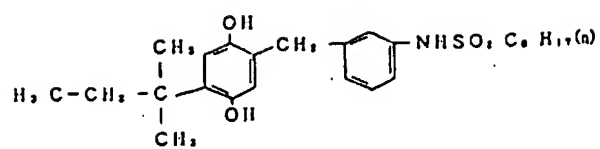
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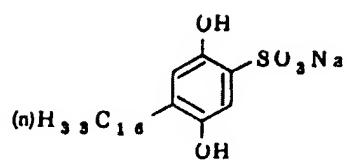
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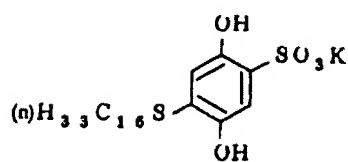
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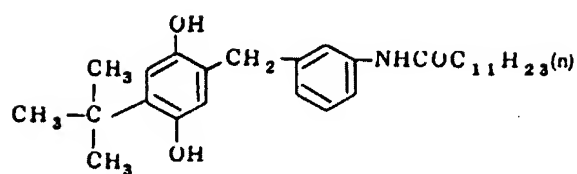
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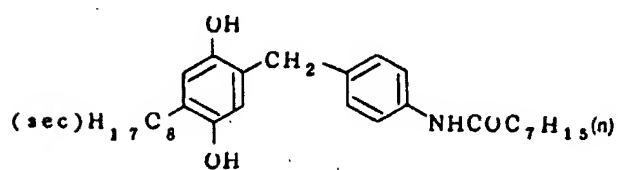
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(ED-9)

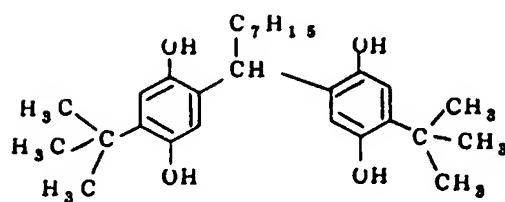


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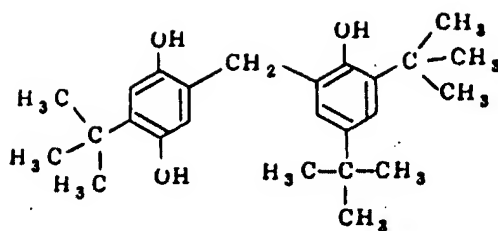


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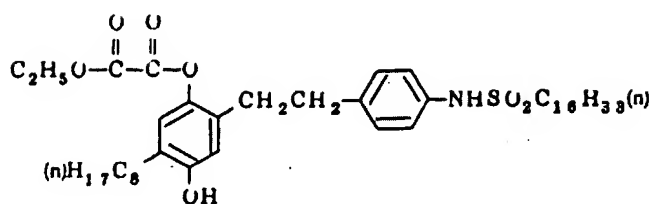
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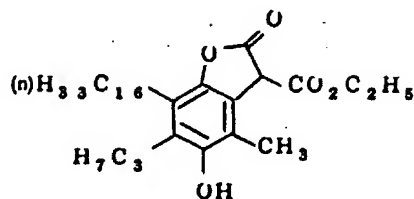
(ED-12)



(ED-13)



(ED-14)



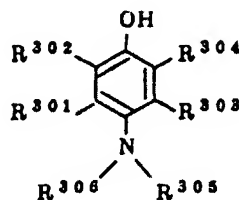
The electron donor (or the precursor thereof) can be used in a wide range of amounts but is preferably in the range of from 0.01 to 50 mol, more preferably from 0.1 to 5 mol, as against 1 mol of the positive dye-providing compound. Further, the amount of the electron donor is in a range of from 0.001 to 5 mol, preferably in a range of from 0.01 to 1.5 mol, as against 1 mol of the silver halide.

The ETA which can be used in combination with the above-mentioned electron donor can be any compounds which are oxidized by silver halide and the oxidation products of which have an

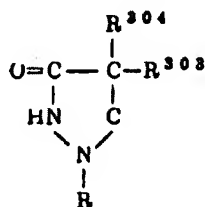
ability of cross-oxidizing the above-mentioned electron donor, and such compounds are preferably mobile.

Particularly preferred examples of ETAs include the compounds represented by the following general formula [X-I] or [X-II]:

[X-I]



[X-II]



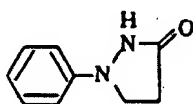
where in R represents an aryl group; R^{301} , R^{302} , R^{303} , R^{304} , R^{305} and R^{306} , which may be the same or different from each other, each represents a hydrogen atom, a halogen atom, an acylamino group, an alkoxy group, an alkylthio group, an alkyl group or an aryl group, each of which, if possible, may be substituted.

In the present invention, the compounds represented by general formula [X-II] are particularly preferred. In general formula [X-II], R^{301} , R^{302} , R^{303} , and R^{304} each preferably represents a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a substituted alkyl group having 1 to 10 carbon atoms or

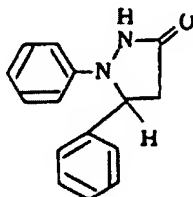
a substituted or unsubstituted aryl group, and each more preferably represents a hydrogen atom, a methyl group, a hydroxymethyl group, a phenyl group or a phenyl group substituted by a hydroxyl group, an alkoxy group, a sulfo group, a carboxyl group, or the like.

Specific examples of ETAs are as follows:

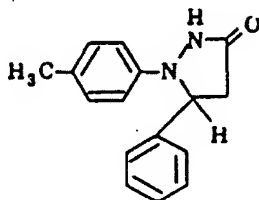
(X-1)



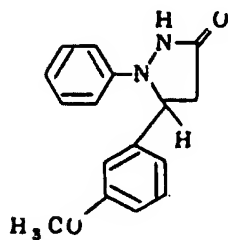
(X-2)



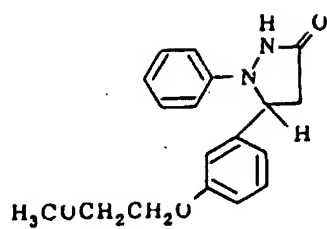
(X-3)



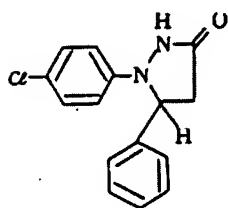
(X-4)



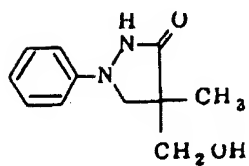
(X-5)



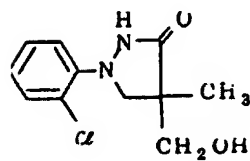
(X-6)



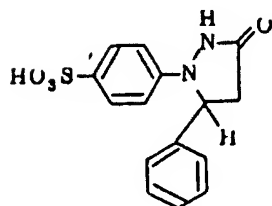
(X-7)



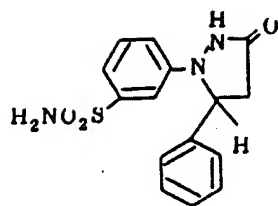
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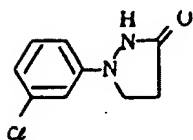
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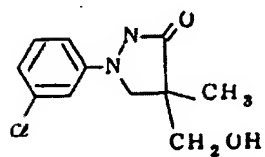
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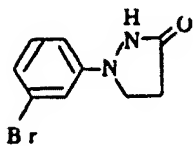
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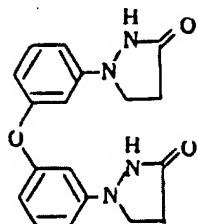
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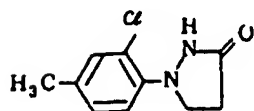
(X-13)



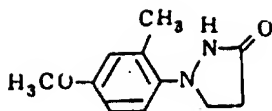
(X-14)



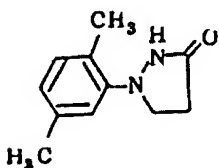
(X-15)



(X-16)



(X-17)



The ETA precursor used in the present invention is a compound which does not have a developing action during the preservation of the light-sensitive material before use but finally releases the ETA by the action of an appropriate activator (e.g., a base and a nucleophilic agent) or the action of heat.

In particular, the ETA precursor used in the present invention does not have a function as an ETA before development because the reactive functional group of the ETA is blocked by a blocking group but functions as an ETA under an alkaline condition or by heating because in this case, the blocking group is cleaved.

Examples of the ETA precursor used in the present invention include 1-phenyl-3-pyrazolidinone-2- or 3-acyl derivatives, 2-aminoalkyl or hydroxyalkyl derivatives, metal salts (e.g., lead salts, cadmium salts, calcium salts and barium salts) of hydroquinone, catechol or the like, halogenated acyl derivatives.

of hydroquinone, oxazine or bisoxazine derivatives of hydroquinone, lactone-type ETA precursors, hydroquinone precursors having a quaternary ammonium group, cyclohex-2-ene-1,4-dione type compounds, compounds releasing an ETA by an electron transfer reaction, compounds releasing an ETA by an intramolecular nucleophilic substitution reaction, ETA precursors blocked by a phthalide group, and ETA precursors blocked by an indomethyl group.

The ETA precursors used in the present invention are known compounds; known examples include the developer precursors described in U.S. Patent. Nos. 3,767,704, 3,241,967, 3,246,988, 3,295,978, 3,462,266, 3,586,506, 3,615,439, 3,650,749, 4,209,580, 4,330,617 and 4,310,612, British Patent Nos. 1,023,701, 1,231,830, 1,258,924, and 1,346,920, Japanese Unexamined Patent Publication Nos. S57-40245, S58-1139, S58-1140, S59-178458, S59-182449 and S59-182450.

/14

In particular, the precursors of 1-phenyl-3-pyrasolidinones described in Japanese Unexamined Patent Publication Nos. S59-178458, S59-182449 and S59-182450 are preferred.

The ETA can be used together with the ETA precursor.

In the present invention, the combination of the electron donor and the ETA is preferably incorporated into the heat-developable color photographic light-sensitive material. Further,

the electron donors and ETAs or the precursors of thereof each can be used as a combination of two or more, and they can be added to each of the emulsion layers (e.g., a blue-sensitive emulsion layer, a green-sensitive emulsion layer, a red-sensitive emulsion layer, an infrared-sensitive emulsion layer, and an ultraviolet-sensitive emulsion layer) of the light-sensitive material, can also be added to specific emulsion layers only, can also be added to a layer adjacent to the emulsion layer (e.g., an anti-halation layer, a subbing layer, an interlayer, and a protective layer), or can also be added to all the layers. The electron donor and ETA can be added to the same layer or can be added separately to separate layers. Further, these reducing agents and the dye-providing compound can be added to the same layer or can be added separately to separate layers, but it is preferred that the non-diffusible electron donor is present in the layer containing the dye-providing compound. The ETA can be incorporated in an image-receiving material (dye-fixing layer) and, when a slight amount of water exists on heat development, the ETA can be dissolved in the water. The preferred amounts of the electron donor and ETA or the precursors thereof are, as the total amounts, 0.01 to 50 mol, preferably 0.1 to 5 mol, as against 1 mol of the dye-providing compound, and are 0.001 to 5 mol, preferably 0.01 to 1.5 mol, as against 1 mol of the silver halide.

Further, the amount of the ETA is 60 mol% or less, and is more preferably 40 mol% or less of the whole amount of the reducing agents. When the ETA is supplied as a solution dissolved in water during processing, the ETA concentration is preferably 10^{-4} mol/L to 1 mol/L.

In order to introduce the reducing substance, the dye-providing compound, the electron donor, the electron transfer agent or the precursors thereof, and other hydrophobic additives into a hydrophilic colloid layer, a high-boiling organic solvent can be used, known examples of which include phthalic acid alkyl esters (e.g., dibutyl phthalate and dioctyl phthalate), phosphoric acid esters (e.g., diphenyl phosphate, triphenyl phosphate, tricyclohexyl phosphate, tricresyl phosphate, and dioctylbutyl phosphate), citric acid esters (e.g., tributyl acetyl-citrate), benzoic acid esters (e.g., octyl benzoate), alkylamides (e.g., diethyl laurylamide), fatty acid esters (e.g., dibutoxy succinate and dioctyl azelate), trimesinic acid esters (e.g., tributyl trimesinate), the carboxylic acids described in Japanese Patent Application No. S61-231500, and the compounds described in Japanese Unexamined Patent Publication No. S59-83154, S59-178451, S59-178452, S59-178453, S59-178454, S59-178455 and S59-178457; in such cases, the method described in U.S. Patent. No. 2,322,027 can be applied or the above-mentioned materials can be dissolved in an organic solvent having a

boiling point of from approximately 30 to 160 degrees Celsius, such as lower alkyl acetates, such as ethyl acetate and butyl acetate, ethyl propionate, secondary butyl alcohol, methyl isobutyl ketone, β -ethoxy ethyl acetate, methylcellosolve acetate, and cyclohexanone, thereby being decomposed to hydrophilic colloid. A mixture of the above-mentioned high-boiling organic solvent and low-boiling organic solvent can be used. Further, after dispersion, as needed, the low-boiling organic solvent can be removed by ultra-filtration or the like. The amount of the high-boiling organic solvent used is 10 g or less, preferably 5 g or less, as against 1 g of the dye-providing compound used. The amount of the high-boiling organic solvent used is 5 g or less, preferably 2 g or less, as against 1 g of the non-diffusible reducing agent. The amount of the high-boiling organic solvent used is 1 g or less, preferably 0.5 g or less, and more preferably 0.3 g or less, as against 1 g of the binder used. The dispersion method by a polymer as described in Japanese Examined Patent Publication No. S51-39853 and Japanese Unexamined Patent Publication No. S51-59943. In addition, the above-mentioned materials can also be directly dispersed in an emulsion, or after dissolving them in water or an alcohol, the resulting solution can be dispersed in a gelatin or an emulsion.

When the compounds are substantially insoluble in water, the compounds can alternatively be dispersed in a binder as fine particles. (e.g., methods as described in Japanese Unexamined Patent Nos. S59-174830 and S53-102733 and Japanese Patent Application No. 62-106882).

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In the case of dispersing hydrophobic substances in a hydrophilic colloid, various surfactants can be used; known examples of surfactants that can be used in this case include those described in Japanese Examined Patent Publication No. S59-157636, pages 37 and 38.

The inventive heat-developable light-sensitive material has a fundamentally light-sensitive silver halide, a binder, an electron donor, an electron transferring agent and a reducible dye-providing compound on a substrate and, as needed, the inventive light-sensitive material can further contain an organic metal salt oxidizing agent. These components usually added to the same layer but can also be separately added to separate layers in the case where the components can be reacted with each other. For example, when the colored dye-providing compound is present in a layer under a silver halide emulsion layer, the reduction of the sensitivity can be prevented. The reducing agent can be preferably incorporated into the heat-developable light-sensitive material but can be provided

externally, for example, by a method wherein the reducing agent is diffused into the light-sensitive material from a dye-fixing material as will be described below.

In order to obtain a wide range of colors in the chromaticity diagram by using three primary colors of yellow, magenta, and cyan, a combination of at least three silver halide emulsion layers each having light sensitivity in a different spectral region can be used. Examples of the combinations that can be applied include a 3 layer combination of a blue-sensitive layer, a green-sensitive layer, and a red-sensitive layer, and a combination of a green-sensitive layer, a red-sensitive layer, and an infrared-sensitive emulsion layer. The light-sensitive layers can be disposed in various disposition orders conventionally employed for ordinary color photographic light-sensitive materials. Further, each light-sensitive layer can be optionally composed of two or more layers.

The inventive heat-developable light-sensitive material can be provided with various subsidiary layers, such as a protective layer, a subbing layer, an intermediate layer, a yellow filter layer, an anti-halation layer and a back layer.

The silver halide used in the present invention can be any of silver chloride, silver bromide, silver iodobromide, silver chlorobromide, silver chloriodide, and silver chloriodobromide.

The silver halide emulsion used in the present invention can be a surface latent image-type emulsion. The term "surface latent image-type emulsion" refers to an emulsion in which latent images are formed on the particle surface and is also referred to "negative emulsion". The definition of the surface latent image-type emulsion is described in Japanese Examined Patent Publication No. S58-9410.

The silver halide emulsion used in the present invention can also be a so-called core/shell-type emulsion wherein the inside of the particles has a different phase from the particle surface layer. The silver halide emulsion can be either a monodisperse silver halide emulsion or a polydisperse silver halide emulsion, and can also be a mixture of monodisperse silver halide emulsions. The particle size of the silver halide particles used in the present invention is preferably 0.1 to 2 μ , and is particularly preferably 0.2 to 1.5 μ . The crystal habit of the silver halide particles can be cubic, octahedral, tetradecahedral, tabular of a high aspect ratio, and the like.

Examples of silver halide emulsions used in the present invention include any of the silver halide emulsions described in U.S. Patent. No. 4,500,626, column 50, U.S. Patent. No. 4,628,021, Research Disclosure ("RD", hereinafter), No. 17029 (1978), and Japanese Unexamined Patent Publication No. S62-253159.

The silver halide emulsion can be used as a primitive emulsion, but is usually chemically sensitized before use. In this case, a sulfur sensitization method, a reduction sensitization method and a noble metal sensitization method, which are known for conventional photographic light-sensitive materials, can be applied alone or in a combination thereof. These chemical sensitizations can be carried out in the presence of a nitrogen-containing heterocyclic compound (as disclosed in Japanese Unexamined Patent Publication No. S62-253159).

The coating amount of the light-sensitive silver halide used in the present invention is in a range of from 1 mg to 10 g/m² on the silver basis.

In the present invention, an organic metal salt can be used as an oxidizing agent together with the light-sensitive silver halide. Of organic metal salts, an organic silver salt can be particularly preferably used.

Examples of organic compounds that can be used to form the above-mentioned organic silver salt oxidizing agents include benzotriazoles, fatty acids and other compounds described in U.S. Patent. No. 4,500,626, columns 52 to 53. Known examples of organic compounds further include silver salts of carboxylic acids having an alkyl group, such as phenyl propiolic acid silver, described in Japanese Unexamined Patent Publication No. S60-113235 and acetylene silver described in Japanese Unexamined

Patent Publication No. S61-249044. These organic silver salts can be used in combination of two or more.

The above-mentioned organic silver salt can be used in an amount of from 0.01 to 10 mol, preferably from 0.01 to 1 mol, as against 1 mol of the light-sensitive silver halide.

/16

The suitable total coating amount of the light-sensitive silver halide and the organic silver salt is from 50 mg to 10 g/m² on the silver basis.

In the present invention, various antifoggants or photographic stabilizers can be used. Examples of such agents include azoles and azaindenes described in RD, No. 17643, pages 24 to 25 (1978), nitrogen-containing carboxylic acids and phosphoric acids described in Japanese Unexamined Patent Publication No. S59-168442, mercapto compounds and the metal salts thereof described in Japanese Unexamined Patent Publication No. S59-111636, and acetylene compounds described in Japanese Unexamined Patent Publication No. S62-87957.

The silver halide used in the present invention can be spectrally sensitized by methine dyes and the like. Examples of such dyes for the spectral sensitization include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes, and hemioxonol dyes.

Specific examples of the sensitizing dyes include those described in U.S. Patent. No, 4,617,257, Japanese Unexamined Patent Nos. S59-180550 and S60-140335, and RD, No. 17029, pages 12 to 13 (1978).

These sensitizing dyes can be used alone or in combination thereof, and a combination of sensitizing dyes is frequently used for the purpose of supersensitization.

In addition to sensitizing dyes, a dye which has no spectral sensitizing action by itself or a compound which does not substantially absorb visible light but shows a supersensitization can be contained in the emulsion (see, for example, those described in U.S. Patent. No. 3,615,641 and Japanese Patent Application S61-226294).

The timing for adding these sensitizing dyes to the emulsion can be before or after the chemical ripening, or before or after the nucleus formation of the silver halide particles according to U.S. Patent Nos. 4,183,756 and 4,225,666. The addition amount of the sensitizing dye is from approximately 1×10^{-8} to 1×10^{-2} mol as against 1 mol of the silver halide.

Hydrophilic binders can be preferably used as a binder for layers constituting the light-sensitive material and dye-fixing material. Examples of such hydrophilic binders include those described in Japanese Unexamined Patent Publication No. S62-253159, pages 26 to 28. More specifically, a transparent or

opaque hydrophilic binder can be preferably used, known examples of which include: natural compounds including proteins, such as gelatin and gelatin derivatives, protein or cellulose derivatives, and polysaccharides, such as starch, gum Arabic, dextran, and pluran; and synthetic high molecular compounds, such as polyvinyl alcohol, polyvinylpyrrolidone and acrylamide polymers. Examples of the binders further include high water-absorptive polymers described in Japanese Unexamined Patent Publication No. S62-245260, i.e., a homopolymer of a vinyl monomer having $-\text{COOM}$ or $-\text{SO}_3\text{M}$ (wherein M represents a hydrogen atom or an alkali metal) and a copolymer of the above vinyl monomers or of the above vinyl monomer and other vinyl monomers (e.g., sodium methacrylate, ammonium methacrylate, and Sumika Gel L-5H, manufactured by Sumitomo Chemical Co., Ltd.). These binders can be used in combination of two or more.

In the case of employing a system of carrying out heat-development by supplying a slight amount of water, the absorption of water can be rapidly conducted by using the above-mentioned high water-absorptive polymer. Further, when the high water-absorptive polymer is used in the dye-fixing layer or a protective layer, the retransfer of dyes from a dye-fixing material to other materials upon completion of the transferring can be prevented.

In the present invention, the coating amount of the binder is preferably 20 g or less, more preferably 10 g or less, and particularly preferably 7 g or less, as against 1 m² of the light sensitive material.

In the layers (including a back layer) constituting the light-sensitive material or the dye-fixing material, various polymer latexes can be contained for the purpose of improving the film properties, such as the dimensional stability, preventing curling, preventing sticking, preventing cracking of layers, and the prevention of the occurrence of pressure sensitization or desensitization. Specific examples of such polymer latexes include any of those described in Japanese Unexamined Patent Publication Nos. S62-245258, S62-136648 and S62-110066. In particular, when a polymer latex having a low glass transition point (40 degrees Celsius or less) is used in a mordant layer, the occurrence of cracking of the mordant layer can be prevented and, when a polymer latex having a high glass transition point is used in a back layer, the curling preventing effect can be obtained.

/17

In this invention, a compound capable of activating the development of, and also stabilizing, the images formed can be used in the light-sensitive material. Preferred examples of such

compounds are described in U.S. Patent. No. 4,500,626, columns 51 to 52.

In the system which forms images by the diffusion transfer of dyes, dye-fixing material is used together with the light-sensitive material. The dye-fixing material and the light-sensitive material can be separately formed on different substrates or can also be formed on the same substrate. The relationship between the light-sensitive material and the dye-fixing material, the relationship between the above materials and substrates, and the relationship between the above materials and a white reflecting layer which are described in U.S. Patent. No. 4,500,626, column 57 can also be applied to the present invention.

The dye-fixing material which can be preferably used in the present invention has at least one layer containing a mordant and a binder. Mordants which are known in the field of photography can be used in the present invention. Specific examples of such mordants include those described in U.S. Patent. No. 4,500,626, columns 58 to 59 and Japanese Unexamined Patent Publication No. S61-88256, pages 32 to 41, and those described in Japanese Unexamined Patent Publication Nos. S62-244043 and S62-244036. Further, the dye-acceptive high molecular compounds as described in U.S. Patent. No. 4,463,079 can also be used in the present invention.

The dye-fixing material can optionally have an auxiliary layer, such as a protective layer, a releasing layer and a curling prevention layer, with the formation of a protective layer being effective.

The layers constituting the light-sensitive material and the dye fixing material can contain a plasticizer, a slipping agent and a high-boiling organic solvent as a release-property improving agent for the dye-fixing material from the light-sensitive material. Specific examples of such agents include those described in Japanese Unexamined Patent Publication No. S62-253159, page 25 and Japanese Unexamined Patent Publication No. S62-245253.

Further, in order to achieve the above object, various silicone oils (including any silicone oils from dimethylsilicone oil to other modified silicone oils obtained by introducing various organic groups to dimethyl siloxane) can be used. Examples of such silicone oils include various modified silicone oils described in "Modified Silicone Oil", Technical Material P6-18B, published by Shin-Etsu Silicone K. K., with carboxymodified silicone (trade name, X-22-3710) being particularly preferred.

Further, the silicone oils described in Japanese Unexamined Patent Publication No. S62-215953 and Japanese Patent Application No. S62-23687 can be effectively used.

The light-sensitive material and the dye-fixing material can contain a discoloration inhibitor. Examples of such a discoloration inhibitor include antioxidants, ultraviolet absorbents and specific types of metal complexes.

Examples of the antioxidants include chroman compounds, coumaran compounds, phenol compounds (e.g., hindered phenols), hydroquinone derivatives, hindered amine derivatives and spiroindane compounds. The compounds described in Japanese Unexamined Patent Publication No. S61-159644 can also be effectively used.

Examples of the ultraviolet absorbents include benzotriazole compounds (e.g., those described in U.S. Patent. No. 3,533,794), 4-thiazolidone compounds (e.g., those described in U.S. Patent. No. 3,352,681), benzophenone compounds (e.g., those described in Japanese Unexamined Patent Publication No. S46-2784), and the compounds described in Japanese Unexamined Patent Publication No. S54-48535, Japanese Unexamined Patent Publication No. S62-136641 and Japanese Unexamined Patent Publication No. S61-88256. Further, the ultraviolet absorptive polymers described in Japanese Unexamined Patent Publication No. S62-260152 can also be effectively used.

Examples of the metal complexes include the compounds described in U.S. Patent. No. 4,241,155, U.S. Patent No. 4,245,018, columns 3 to 36, U.S. Patent No. 4,254,195, columns 3

to 8, Japanese Unexamined Patent Publication No. S62-174741, Japanese Unexamined Patent Publication No. S61-88256, pages 27 to 29, Japanese Patent Application No. 62-234103, Japanese Patent Application No. S62-31096 and Japanese Patent Application No. S62-23059.

Examples of effective discoloration inhibitors are described in Japanese Unexamined Patent Publication No. S62-215272, pages 125 to 137.

The discoloration inhibitors which inhibit the dyes transferred to the dye-fixing material can be contained in the dye-fixing material, or can also be provided externally, for example, from the light-sensitive material.

/18

The above-mentioned antioxidants, ultraviolet absorbents and metal complexes can be used in combination.

Brightening agents can be used in the light-sensitive material and the dye-fixing material. In particular, it is preferred that the brightening agent is incorporated into the dye-fixing material or is provided externally, for example, from the light-sensitive material. Examples of such brightening agents include compounds described in K. Veenkataraman, "the Chemistry of Synthetic Dyes", Vol. V, Chapter 8, and Japanese Unexamined Patent Publication No. S61-143752. Specific examples of the compounds include stilbene compounds, coumarin compounds,

biphenyl compounds, benzoxazolyl compounds, naphthalimide compounds, pyrazolidone compounds and carbostyryl compounds.

The brightening agent can be used in combination with a discoloration inhibitor.

Examples of hardening agents that can be used in the layers constituting the light-sensitive material and the dye-fixing material include those described in U.S. Patent. No. 4,678,739, column 41, Japanese Unexamined Patent Publication No. S59-116655, Japanese Unexamined Patent Publication No. S62-245261 and Japanese Unexamined Patent Publication No. S61-18942. Specific examples of the hardening agents include aldehyde hardening agents (e.g., formaldehyde), aziridine hardening agents, epoxy series hardening agents (e.g., $\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-(\text{CH}_2)_n-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2$), vinylsulfone hardening agents [e.g., N,N'-ethylene-bis(vinylsulfonylacetamido)ethane], N-methylol hardening agents (e.g., dimethylolurea) and high molecular hardening agents (e.g., the compounds described in Japanese Unexamined Patent Publication No. S62-234157).

The layers constituting the light-sensitive material or the dye fixing material can contain various surfactants as coating aids and in order to improve the releasability and slipping properties, provide the antistatic properties and accelerate the development. Specific examples of surfactants are described in

Japanese Unexamined Patent Publication No. S62-173463 and Japanese Unexamined Patent Publication No. S62-183457.

The layers constituting the light-sensitive material and the dye-fixing material can contain an organic fluoro compound in order to improve the slipping properties, providing the antistatic properties and improve the releasability. Typical examples of organic fluoro compounds the fluorine surfactants described in Japanese Examined Patent Publication No. S57-9053, columns 8 to 17, Japanese Unexamined Patent Publication No. S61-20944 and Japanese Unexamined Patent Publication No. S62-135826, and hydrophobic fluorine compounds, such as oily fluorine compounds, such as fluorine oil, and solid fluorine compound resins, such as tetrafluoroethylene resin.

Matting agents can be used in the light-sensitive material and dye-fixing material. Examples of matting agents include the compounds described in Japanese Unexamined Patent Publication No. S61-88256, page 29, such as silicon dioxide, polyolefin and polymethacrylate, and the compounds described in Japanese Patent Application No. 62-110064 and Japanese Patent Application No. S62-110065, such as benzoguanamine resin beads, polycarbonate resin beads and AS resin beads.

In addition, the layers constituting the light-sensitive material and the dye-fixing material can further contain a thermal solvent, a defoaming agent, an antibacterial/antifungal

agent, colloidal silica and the like. Specific examples of such agents are described in Japanese Unexamined Patent Publication No. S61-88256, pages 26 to 32.

Image formation accelerators can be used in the light-sensitive material and/or the dye-fixing material. Image formation accelerators have the functions of accelerating the oxidation reduction reaction of the silver salt oxidizing agent and the reducing agent, accelerating the reaction of forming dyes from the dye-providing compounds, decomposing dyes, or releasing diffusible dyes, and accelerating the transfer of dyes from the light-sensitive layers to the dye-fixing layer. From the standpoint of physicochemical functions, the image formation accelerators are classified into compounds which have co-actions with bases/base precursors, nucleophilic compounds, high-boiling organic solvents (oils), thermal solvents, surfactants, and silver/silver ions. However, these substances generally have composite functions and usually have two or more of the above-mentioned acceleration effects. Details of the substances are described in U.S. Patent. No. 4,678,739, columns 38 to 40.

Examples of the base precursors include a salt of a base and an organic acid causing decarboxylation by heat and compounds capable of releasing amines by an intramolecular nucleophilic substitution reaction, a Lossen rearrangement or a Beckmann rearrangement. Specific examples of the base precursors

are described in U.S. Patent No. 4,511,493 and Japanese Unexamined Patent Publication No. S62-65038.

/19

In the system which simultaneously carries out the heat development and the transfer of dyes in the presence of a small amount of water, it is preferred that the base and/or the base precursor are contained in the dye-fixing material in order to improve the storage properties of the light-sensitive material.

In addition, examples of compounds that can also be used as base precursors further include the combination of poorly water-soluble metal compounds and compounds (i.e., complex-forming compounds) capable of causing a complex-forming reaction with the metal ions forming the poorly water-soluble compounds as described in European Patent No. 210,660, and the compounds which form a base by electrolysis as described in Japanese Unexamined Patent Publication No. S61-232451. In particular, the former method is effective. It is effective that the poorly water-soluble metal compound and the complex-forming compound are separately incorporated into the light-sensitive material and the dye-fixing material, respectively.

Various development terminators can be used in the light-sensitive material and/or the dye-fixing material according to the present invention in order to constantly obtain stable

images against the variations of the processing temperature and the processing time on development.

The term "development terminator" as used herein refers to a compound which rapidly neutralizes a base or is reacted with a base after the appropriate development in order to reduce the concentration of the base in the layers, thereby terminating the development, or a compound which is capable of causing a co-action with silver and a silver salt in order to restrain the development. Specific examples of such development terminators include acid precursors which release an acid by heating, electrophilic compounds which cause a substitution reaction with a co-existing base by heating, nitrogen-containing heterocyclic compounds, mercapto compounds, and precursors thereof. Details of these compounds are described in Japanese Unexamined Patent Publication No. S62-253159, pages 31 to 32.

A substrate which withstands the processing temperature can be used as a substrate for the light-sensitive material and the dye-fixing material in the present invention. Materials generally used are paper sheets and synthetic polymers (films). Specific examples of the materials include polyethylene terephthalate, polycarbonate, polyvinyl chloride, polystyrene, polypropylene, polyimide, celluloses (e.g., triacetyl cellulose), the materials obtained by incorporating a pigment, such as titanium oxide, into the above-mentioned films, synthetic paper

sheets formed by polypropylene or the like, papers made of a mixture of a synthetic resin pulp, such as polyethylene, and a natural pulp, Yankee paper sheets, baryta-coated paper sheets, coated paper sheets (in particular, cast coating paper sheets), metal sheets, cloths and glass sheets.

These paper sheets can be used alone or as a coated paper, one surface or both surfaces of which are coated with a synthetic polymer, such as polyethylene.

Further, the substrates as described in Japanese Unexamined Patent Publication No. S62-253159, pages 29 to 31, can also be used.

The surface of the substrate can also be coated with a mixture of a hydrophilic binder and a semiconductive metal oxide, such as an alumina sol and tin oxide, and an antistatic agent, such as carbon black.

Examples of methods for imagewise exposing the light-sensitive material include a method wherein a scene, a person and the like are directly photographed using a camera, a method wherein images are exposed through a reversal film or a negative film using a printer, an enlarger or the like, a method wherein original images are scanning-exposed through a slit or the like using an exposure device of a copying machine, a method wherein images are exposed to light emitted from a light emitting diode or various lasers through electric signals according to an image

information, and a method wherein image information is output on an image display device, such as a CRT, a liquid crystal display, an electroluminescence display, a plasma display or the like in order to expose the displayed images directly to light or through an optical system.

Examples of light sources for recording images to the light-sensitive material include natural light, a tungsten lamp, a light emitting diode, a laser light source, and a CRT light source and the like as described in U.S. Patent. No. 4,500,626, column 56.

Further, the image-exposure can also be applied by using a wavelength conversion element which is composed of a combination of a non-linear optical material and a coherent light source, such as laser light. The term "non-linear optical material" as used herein refers to a material which is capable of generating a non linearity between the polarization and the electric field appearing on applying a strong photoelectric field, such as laser light; preferred examples of such materials include inorganic compounds, typified by lithium niobate, potassium dihydrogenphosphate (KDP), lithium iodate and BaB_2O_4 , urea derivatives, nitroaniline derivatives, nitropyridine-N-oxide derivatives, such as 3-methyl-4-nitropyridine-N-oxide (POM), and the compounds described in Japanese Unexamined Patent Publication No. S61-53462

and Japanese Unexamined Patent Publication No. S62-210432. Known examples of the form of wavelength conversion element include a single crystal light waveguide form and a fiber form, and any of these can be effectively used.

Examples of the image signals that for the above-mentioned information include an image signal obtained from a video camera, electron still camera or the like, a television signal, typified by Nippon Television Signal Code (NTSC), an image signal obtained by dividing an original into many dots by using a scanner or the like, and an image signal made by using a computer, typified by CG and CAD.

The light-sensitive material and/or the dye-fixing material can be in the form having a conductive exothermic layer as a heating means for the development of heat or the diffusion transfer of dyes. In this case, the transparent or opaque exothermic elements described in Japanese Unexamined Patent Publication No. S61-145544 can be used. The conductive layer also functions as an antistatic layer.

The heating temperature in the heat development step is from approximately 50 degrees Celsius to approximately 25 [sic] degrees Celsius but, in particular, a temperature range of from preferably approximately 80 degrees Celsius to approximately 180 degrees Celsius is effective. The diffusion transfer step for

dyes can be carried out simultaneously with the heat development, or can also be carried out on completion of the heat development step. In the latter case, the heating temperature in the transfer step can range from room temperature to a temperature in the heat development step, but the heating temperature is preferably in the range of from approximately 50 degrees Celsius to a temperature 10 degrees Celsius lower than the temperature in the heat development step.

The transfer of dyes can occur by heat only, but a solvent can be used in order to accelerate the transfer of dyes.

Further, as described in detail in Japanese Unexamined Patent Publication No. S59-218443 and Japanese Unexamined Patent Publication No. S61-238056, a method of heating in the presence of a small amount of a solvent (in particular, water) to carry out the development and the transfer of dyes simultaneously or in succession can be effectively applied in the present invention. In this method, the heating temperature is preferably in a range of from 50 degrees Celsius or more to the boiling point of the solvent or less. For example, when the solvent is water, the heating temperature is preferably from 50 degrees Celsius or less to 100 degrees Celsius or less.

Examples of solvent which can be used to accelerate the development and/or the transfer of diffusible dyes to the dye-fixing layer include water and basic aqueous solutions of an

inorganic alkali metal salt or an organic base (examples of the base include those described above on the image formation accelerators). Examples of solvents further include a low-boiling solvent and a mixture of a low-boiling solvent and water or the basic aqueous solution can be used. Further, the solvent can contain surfactants, antifoggants, poorly water-soluble metal salts, complex-forming compounds and the like.

These solvents can be used by adding them to the dye-fixing material and/or the light-sensitive material. The amount of the solvent used can be a small amount which is smaller than the weight of the solvent corresponding to the maximum swelled volume of the total coated layers (in particular, smaller than the amount obtained by subtracting the weight of the total coated layers from the weight of the solvent corresponding to the maximum swelled volume of the total coated layers).

Examples of application methods of a solvent to the light-sensitive layer or the dye-fixing layer include the method described in Japanese Unexamined Patent Publication No. S61-147244, page 26. Further, the solvent can be incorporated in advance in the light-sensitive material and/or the dye-fixing material, for example, by encapsulating the solvent in microcapsules.

In order to accelerate the dye transfer, a system which incorporates a hydrophilic thermal solvent, which is in the form

of a solid at room temperature but is melted at a high temperature, into the light-sensitive material or the dye-fixing material can be employed. The hydrophilic thermal solvent can be present in either the light-sensitive material or the dye-fixing material or in both materials. The hydrophilic thermal solvent can be incorporated into any of an emulsion layer, an intermediate layer, a protective layer and a dye-fixing layer, but the incorporation into the dye-fixing layer and/or a layer adjacent to the dye-fixing layer are particularly preferred.

Examples of the hydrophilic thermal solvent include ureas, pyridines, amides, sulfonamides, imides, alcohols, oximes, and heterocyclics.

Further, in order to accelerate the dye transfer, a high-boiling organic solvent can be incorporated into the light-sensitive material and/or the dye-fixing material.

Examples of heating methods in the heat development step and/or the dye transfer step include a method wherein there is contact with a heated block or plate, a method wherein there is contact with a hot plate, a hot presser, a heat roller, a halogen lamp heater, an infrared or far infrared lamp heater or the like, and a method involving passing through a high-temperature atmosphere.

In the case of superposing the dye-fixing material onto the light-sensitive material and applying a pressure to the assembly

for the purpose of closely superposing them, the pressing method and the pressing conditions as described in

/21

Japanese Unexamined Patent Publication No. S61-147244, page 27 can be suitably employed in the present invention.

Various heat developing apparatuses can be used for the treatment of the photographic elements according to the present invention. Preferred examples of such apparatuses include those described in Japanese Unexamined Patent Publication No. S59-75247, Japanese Unexamined Patent Publication No. S59-177547, Japanese Unexamined Patent Publication No. S59-181353, Japanese Unexamined Patent Publication No. S60-18951, and Japanese Unexamined Utility Model Application Publication No. S62-25944.

[Embodiments]

The present invention is described with reference to embodiments below.

<Embodiment 1>

The preparation of the emulsion (I) for Layer 1 is described.

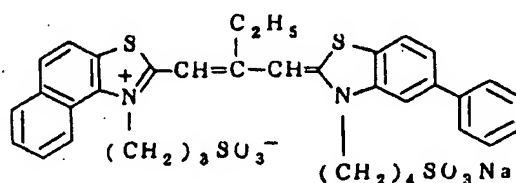
The following solution (I), solution (II) and solution (III) were simultaneously added to an aqueous gelatin solution (prepared by adding 20 g of gelatin, 1 g of potassium bromide and 0.5 g of $\text{OH}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{OH}$ to 800 mL of water and maintaining the solution at a temperature of 50 degrees Celsius) at the same

feed rate for over 30 minutes while the solution was being thoroughly stirred, thereby preparing a monodispersed silver bromide emulsion to which a dye having an average particle size of 0.42 μ had been adsorbed.

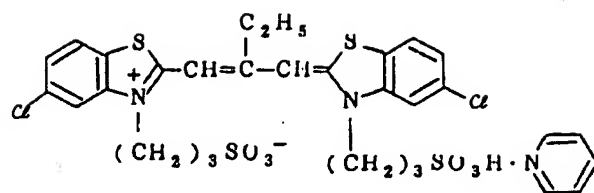
After the resulting emulsion had been washed with water and desalted, 20 g of lime-processed ossein gelatin was added thereto, and after adjusting the pH to 6.4 and pAg to 8.2, the resulting mixture was heated at a temperature of 60 degrees Celsius, 9 mg of sodium thiosulfate, 6 mL of 0.01% chloroauric acid aqueous solution and 190 mg of 4-hydroxy 6-methyl-1,3,3a-7-tetraazaindene were added thereto, and the resulting emulsion was chemically sensitized for 45 minutes, with the yield of the emulsion being 635 g.

	Solution I (Total 450 mL with water)	Solution II (Total 400 mL with water)	Solution III (Total 60 mL with methanol)
AgNO ₃	100 g	-	-
KBr	-	70 g	-
Dye (a)	-	-	40 mg
Dye (b)	-	-	80 mg

Dye (a)



Dye (b)



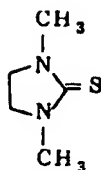
The preparation of the emulsion (II) for Layer 3 is described.

The following solution (I) and solution (II) were simultaneously added to an aqueous solution (prepared by adding 20 mg of gelatin, 0.30 g of potassium bromide, 6 g of sodium chloride and 0.015 g of the chemical A shown below to 730 mL of water and maintaining the solution at a temperature of 60 degrees Celsius) at the same feed rate for over 60 minutes while the solution was being thoroughly stirred. Upon completion of the addition of the solution (I), a methanol solution (III) of the following sensitizing dye was added to the solution. A monodispersed cubic emulsion to which a dye having an average particle size of 0.45 μ had been adsorbed was thereby obtained.

After the resulting emulsion had been washed with water and desalted, 20 g of gelatin was added thereto, and after adjusting the pH to 6.4 and pAg to 7.8, the resulting emulsion was chemically sensitized at a temperature of 60 degrees Celsius. The chemicals used in this case were 1.6 mg of triethylthiourea and 100 mg of 4-hydroxy-6-methyl-1,3,3a-7-tetraazaindene, with

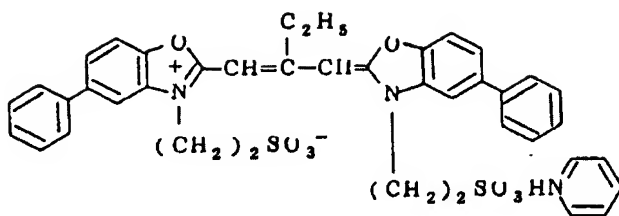
the ageting time being 55 minutes and the yield of the emulsion being 653 g.

(Chemical A)



/22

(Sensitizing dye C)



	Solution I (Total 440 mL with water)	Solution II (Total 400 mL with water)	Solution III (Total 77 mL with methanol)
AgNO ₃	100.0 g	-	-
KBr	-	56.0 g	-
NaCl	-	7.2 g	-
Dye C	-	-	0.23 mg

The preparation of the emulsion (III) for Layer 5 is described.

The following solution (I) and solution (II) were simultaneously added to a gelatin aqueous solution (prepared by adding 30 g of gelatin, 3 g of potassium bromide and 0.5 g of HO(CH₂)₂S(CH₂)₂S(CH₂)₂OH to 600 mL of water and maintaining the solution at a temperature of 65 degrees Celsius) at the same feed rate for over 20 minutes while the solution was being thoroughly stirred. Thereafter, the following solution (III) and

solution (IV) were simultaneously added thereto for over 30 minutes. After the resulting emulsion had been washed with water, 20 g of lime-processed ossein gelatin was added thereto, and after adjusting the pH to 6.2 and pAg to 8.5, sodium thiosulfate, chloroauric acid and 4-hydroxy 6-methyl-1,3,3a-7-tetraazaindene were added thereto in order to carry out an optimal chemical sensitization. Therefore, 600 g of a monodispersed octahedral silver bromide emulsion (15) having an average particle size of 0.5 μm was obtained.

	Solution I (Total 200 mL with water)	Solution II (Total 200 mL with water)	Solution III (Total 400 mL with water)	Solution IV (Total 400 mL with water)
AgNO ₃ (g)	30	-	70	-
KBr (g)	-	19	-	49
HI (g)	-	1.5	-	-

Next, the preparation of gelatin dispersion of a dye-providing compound is described. 20 g of yellow dye-providing compound (1), 13.6 g of electron donor (ED-9), and 10 g of tricyclohexyl phosphate were weighted and added to 57 mL of ethyl acetate, the resulting mixture was melted by heating it at a temperature of approximately 60 degrees Celsius so as to obtain a homogeneous solution. 110 g of an aqueous 10% lime-processed gelatin solution, 65 mL of water and 1.7 g of sodium dodecylbenzenesulfonate were added to the resulting solution with stirring, and the resulting mixture was dispersed by using a homogenizer at a rotational ratio of 10,000 rpm for 10 minutes.

The resulting dispersion liquid was taken as a dispersion of the yellow dye-providing compound.

Dispersions of magenta and cyan dye-providing compounds were prepared by the same method as the dispersion of the yellow dye-providing compound, except that a magenta dye-providing compound (2) or a cyan dye-providing compound (16) was used.

With these products thus obtained, a color photographic light-sensitive material 101 having multiple layers shown in Table 1 was obtained.

/23

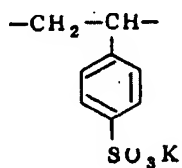
<Table 1>

Layer No.	Layer name		Proportion (g/m ²)
Layer 6	Protective layer	Gelatin	0.92
		Zn(OH) ₂	0.46
		Matting agent (silica)	0.03
		Water-soluble polymer (1)*	0.02
		Surfactant (1)*	0.06
		Surfactant (2)*	0.13
		Hardening agent (1)*	0.01
Layer 5	Blue light-sensitive layer	Emulsion (III)	0.35 on silver basis
		Gelatin	0.48
		Sensitizing dye (d)	2.50×10 ⁻³
		Antifoggant (1)*	5.00×10 ⁻⁴
		Yellow dye-providing substance (1)	0.41
		High-boiling organic solvent (1)*	0.21
		Electron donor (ED-9)	0.28
		Surfactant (3)*	0.05
		Electron transferring agent (X-2)	0.04
		Hardening agent (1)*	0.004
		Water-soluble polymer (1)*	0.01
Layer 4	Intermediate layer	Gelatin	0.70
		Surfactant (1)*	0.02
		Surfactant (3)*	0.01
		Surfactant (4)*	0.06
		Water-soluble polymer (1)*	0.02
		Reducing agent (1)*	0.19
		Polymer (1)*	0.09
Layer 3	Green light-sensitive layer	Hardening agent (1)*	0.008
		Emulsion (II)	0.21 on silver basis
		Gelatin	0.30
		Antifoggant (2)*	6.4×10 ⁻⁴
		Magenta dye-providing substance (2)	0.32
		High-boiling organic solvent (1)*	0.16
		Electron donor (ED-9)	0.12

		Surfactant (3)	0.03
		Electron transferring agent (X-2)	0.04
		Hardening agent (1)*	0.003
		Water-soluble polymer (1)*	0.01
Layer 2	Intermediate layer	Gelatin	0.79
		Matting layer (silica)	0.008
		Zn(OH) ₂	0.46
		Surfactant (1)*	0.05
		Surfactant (4)*	0.10
		Water-soluble polymer (1)*	0.03
		Hardening agent (1)*	0.009
Layer 1	Red light-sensitive layer	Emulsion (I)	0.21 on silver basis
		Gelatin	0.30
		Antifoggant (2)*	6.4×10 ⁻⁴
		Cyan dye-providing substance (9)	0.28
		High-boiling organic solvent (1)*	0.14
		Electron donor (ED-9)	0.16
		Surfactant (3)*	0.03
		Electron transferring agent (X-2)	0.04
		Hardening agent (1)*	0.003
		Water-soluble polymer (1)*	0.01
Substrate (polyethylene terephthalate; thickness 100μ)			
Back layer		Carbon black	0.44
		Polyester	0.30
		Polyvinylchloride	0.30

/24

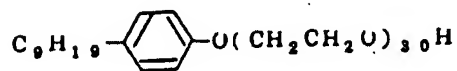
Water-soluble polymer (1)*



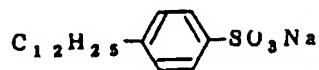
Surfactant (1)*

Aerosol OT

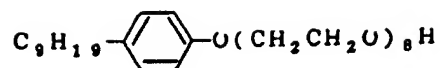
Surfactant (2)*



Surfactant (3)*



Surfactant (4)*



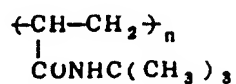
Hardening agent (1)*

1,2-bis(vinylsulfonylacetoamide)ethane

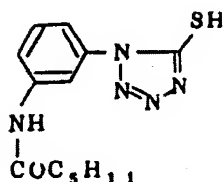
High-boiling organic solvent (1)*

Tricyclohexyl phosphate

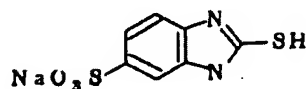
Polymer (1)*



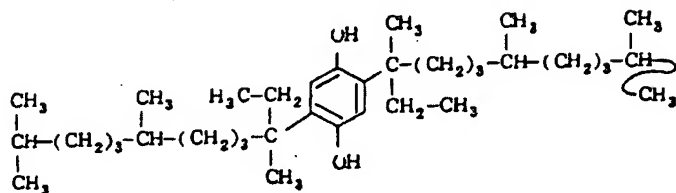
Antifoggant (1)*



Antifoggant (2)*



Reducing agent (1)*



Preparation of the dye-fixing material is described below.

A dye-fixing material R-1 having the following structure on a paper substrate coated with polyethylene was prepared.

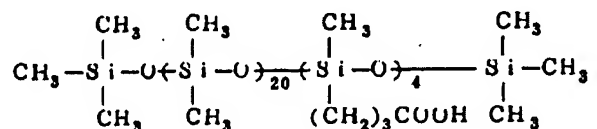
Table 2: Structure of dye-fixing material R-1

Layer No.	Additives	Proportions (g/m ²)
Layer 3	Gelatin	0.05
	Matting agent (silica)	0.02
	Silicone oil* ¹	0.4
	Surfactant* ²	0.001
	Surfactant* ³	0.02
	Surfactant* ⁴	0.10
Layer No.	Additives	Proportions (g/m ²)
Layer 3	Guanidine picolinate	0.45
	Polymer* ³	0.24
Layer 2	Mordant* ⁶	2.35
	Polymer* ⁷	0.60
	Gelatin	1.40
	Polymer* ⁵	0.21
	High-polymer solvent* ⁶	1.40
	Guanidine picolinate	1.80
	Surfactant* ²	0.02
Layer 1	Gelatin	0.45
	Surfactant* ⁴	0.01
	Polymer* ⁵	0.04
	Hardening agent* ⁷	0.30
Paper substrate coated with polyethylene (thickness 170 μ)		
Back Layer 1	Gelatin	3.25
	Hardening agent* ⁹	0.25

/25

Layer No.	Additives	Proportions (g/m ²)
Back Layer 2	Gelatin	0.44
	Silicone oil* ¹	0.08
	Surfactant* ⁵	0.002
	Matting agent* ¹⁰	0.09

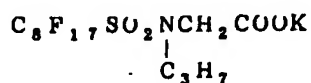
Silicon oil*¹



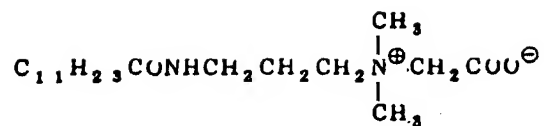
Surfactant*²

Aerosol OT

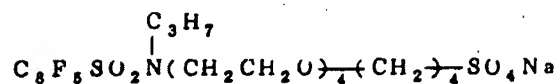
Surfactant*³



Surfactant*⁴



Surfactant*⁵



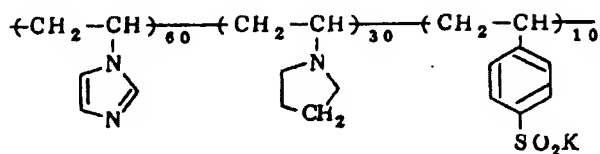
Polymer*⁵

Vinyl alcohol/sodium acrylate copolymer (molar ratio 75/25)

Polymer*⁷

Dextran (molecular weight 70,000)

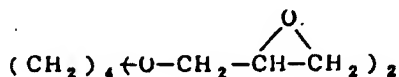
Mordant*⁶



High-boiling organic solvent*⁸

REOFOS 95 (manufactured by Ajinomoto Co., Ltd.)

Hardening agent*⁹



Matting agent*¹⁰

Benzoguanamine resin (average particle diameter 15 μ)

Next, as shown in the following [Table 2], heat-developable light-sensitive materials 102 to 108 were prepared having the same composition as the light-sensitive material 101, except

that compounds AS-1, 12, 4 or 17 as described in the examples were added or the amount of the above-mentioned electron transferring agent (X-2) increased.

[Table 2]

Light-sensitive material No.	Additives	Adding layers	Proportion of each layer (g/m ²)
102	AS-1	1, 3, 5	0.03
103	AS-1	2, 4	0.05
104	AS-12	1, 3, 5	0.065
105	AS-12	2, 4	0.10
106	AS-4	1, 3, 5	0.035
107	AS-17	1, 3, 5	0.055
108	Electron transferring agent (X-2)	1, 3, 5	0.02

Each of the above color photographic light-sensitive materials was exposed to a tungsten lamp for 1/10 second at an intensity of 5,000 lux through a B, G, R, or grey color separation filter having continuously changing densities.

While the thus exposed light-sensitive material was being fed at a line speed of 20 mm/sec., 15 mL/m² of water was provided on the emulsion layer surface by using a wire bar and, immediately thereafter, the light-sensitive material was superposed on the image-receiving material.

/26

The assembly was heated for 15 seconds using a heat roller having a controlled temperature such that the temperature of the water-absorbed layer became 85 degrees Celsius. Thereafter, when the image-receiving material was separated from the light-

sensitive material, clear blue, green, red, and grey images were obtained on the image-receiving material without unevenness corresponding to the B, G, R and grey separation filters.

The maximum density (Dmax) and the minimum density (Dmin) of each of the cyan, magenta, and yellow colors in the grey portion were measured, the results being shown in [Table 3].

[Table 3]

Light-sensitive materials	Dmax			Dmin		
	Cyan	Magenta	Yellow	Cyan	Magenta	Yellow
101	2.10	2.20	2.06	0.17	0.18	0.19
102	2.09	2.20	2.05	0.13	0.12	0.14
103	2.11	2.19	2.03	0.13	0.13	0.14
104	2.09	2.19	2.07	0.12	0.12	0.13
105	2.08	2.22	2.05	0.12	0.13	0.13
106	2.11	2.21	2.06	0.13	0.12	0.14
107	2.10	2.21	2.07	0.12	0.13	0.13
108	2.08	2.18	2.04	0.15	0.16	0.17

As shown in [Table 3], the stains in the color image were reduced in the light-sensitive materials 102 to 107 in which the inventive compounds had been used. The light-sensitive material 108 containing a reducing agent besides the reducing agent represented by general formula [I] according to the present invention (i.e., the amount of the electron transferring agent (X-2) had been increased), had a small reducing effect of image stains and the value of Dmax was significantly reduced.

<Embodiment 2>

A color photographic light-sensitive material 201 having the multilayer structure shown in the following table was

prepared using the same silver halide emulsions, dye-providing compounds, electron donors and electron transferring agents as in the color photographic light-sensitive material 101 in Embodiment 1. [Table 4]

The additives used were the same as those for the light-sensitive material 101, unless otherwise indicated.

The organic silver salt emulsion was prepared as follows:

20 g of gelatin and 5.9 g of 4-acetylamino-phenylpropionic acid were dissolved in a mixture of 1000 mL of an aqueous solution of 0.1% sodium hydroxide and 200 mL of ethanol, and the resulting solution was stirred at a temperature of 40 degrees Celsius. The resulting solution was stirred while the temperature was maintained at 40 degrees Celsius. A solution obtained by adding 4.5 g of silver nitrate to 200 mL of water was added to the resulting solution over a period of 5 minutes. Next, excess salt was removed by a sedimentation method. Thereafter, the pH thereof was adjusted to 6.3, thereby obtaining the organic silver salt emulsion having a yield of 300 g.

Further, an antifoggant precursor (1)*¹ having the following structure was added in an amount of 0.2 mol times the amount of the dye-providing compound and was used together with the dye-providing compound and the electron donor as the oil dispersion as in Embodiment 1.

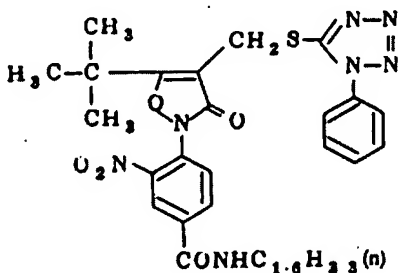
[Table 4]

Layer No.	Layer name		Proportion (g/m ²)
Layer 6	Protective layer	Gelatin	0.91
		Matting agent (silica)	0.03
		Surfactant (1)*	0.06
		Surfactant (2)*	0.13
		Hardening agent (1)*	0.01
		Base precursor (1)*	0.30
Layer 5	Blue light-sensitive layer	Emulsion (III)	0.30 on silver basis
		Organic silver salt emulsion	0.25 on silver basis
		Gelatin	1.00
		Antifoggant (1)*	0.07
		Yellow dye-providing substance (1)	0.50
		High-boiling organic solvent (1)*	0.75
		Electron donor (ED-12)	0.35
		Surfactant (3)*	0.05
		Electron transferring agent (X-5)	0.04
		Thermal solvent (1)*	0.20
		Hardening agent (1)*	0.01
		Base precursor (1)*	0.27
Layer 4	Intermediate layer	Water-soluble polymer (1)*	0.02
		Gelatin	0.75
		Reducing agent (2)*	0.24
		Surfactant (1)*	0.02
		Surfactant (4)*	0.07
		Water-soluble polymer (1)*	0.02
Layer 3	Green light-sensitive layer	Hardening agent (1)*	0.01
		Basic precursor (1)*	0.25
		Emulsion (II)	0.20 on silver basis
		Organic silver salt emulsion	0.20 on silver basis
		Gelatin	0.85
		Antifoggant precursor (1)*	0.04
		Magenta dye-providing substance (2)	0.37
		High-boiling organic solvent (1)*	0.55
		Electron donor (ED-12)	0.20
		Surfactant (3)*	0.04
		Electron transferring agent (X-5)	0.04
		Thermal solvent (1)*	0.16
Layer 2	Intermediate layer	Hardening agent (1)*	0.01
		Basic precursor (1)*	0.25
		Water-soluble polymer (1)*	0.03
		Surfactant (4)*	0.10
		Surfactant (1)*	0.06
		Reducing agent (2)*	0.24
Layer 1	Red light-sensitive layer	Gelatin	0.80
		Emulsion (I)	0.20 on silver basis
		Organic silver salt emulsion	0.20 on silver basis
		Sensitizing dye (1)*	1.07×10 ⁻³
		Gelatin	0.85
		Antifoggant precursor (1)*	0.04
		Thermal solvent (1)*	0.16
		Basic precursor (1)*	0.25
		Cyan dye-providing substance (9)	0.40
		High-boiling organic solvent (1)*	0.60

	Electron donor (ED-12)	0.20
	Surfactant (3)*	0.04
	Electron transferring agent (X-5)	0.04
	Hardening agent (1)*	0.01
	Water-soluble polymer (1)*	0.02
Substrate (polyethylene terephthalate; thickness 100 μ)		
Back layer	Carbon black	0.44
	Polyester	0.30
	Polyvinylchloride	0.30

/28

Antifoggant precursor (1)*



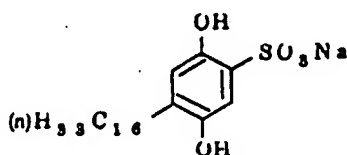
Thermal solvent (1)*

Benzenesulfonamine

Base precursor (1)*

4-chlorophenylsulfonyl guanidine acetate

Reducing agent (2)*



The preparation of a dye-fixing material (R-2) is described below.

10 g of poly(methyl acrylate-co-N,N,N-trimethyl-N-vinylbenzylammonium chloride) (ratio of methyl acrylate to vinylbenzylammonium chloride 1:1) was dissolved in 200 mL of water, the resulting solution was uniformly mixed with 100 g of

an aqueous solution of 10% lime-processed gelatin. After adding a hardening agent to the mixture, the mixture was uniformly applied to a paper substrate coated with polyethylene in which titanium dioxide had been dispersed at a wet thickness of 90 μm . The sample was dried and used as a dye-fixing material (R-2) having a mordant layer.

Light-sensitive materials 202 to 207 having the same compositions of the light-sensitive material 201, except that the compounds according to the present invention were added to the light-sensitive material 201 as shown in [Table 5].

[Table 5]

Light-sensitive material No.	Additives	Adding layers	Proportion of each layer (g/m ²)
202	AS-1	1, 3, 5	0.03
203	AS-1	2, 4	0.05
204	AS-12	1, 3, 5	0.065
205	AS-12	2, 4	0.10
206	AS-4	1, 3, 5	0.035
207	AS-17	1, 3, 5	0.055

After exposing each of the light-sensitive materials thus prepared by the same method as Embodiment 1, the light-sensitive materials were uniformly heated on a heat block having a heated temperature of 140 degrees Celsius for 30 seconds.

After providing 20 mL per 1 m² of water to the layer surface side of the dye-fixing material (R-2), the above-mentioned light-sensitive material thus heated was superposed to the dye-fixing material such that the layers were brought into contact with each other.

Thereafter, after passing the assembly through a laminator heated to a temperature of 80 degrees Celsius at a line speed of 12 mm/sec., the dye-fixing material was separated from the light-sensitive material. In each case, positive images having a desired S/N ratio were obtained on the dye-fixing material.

The results of measuring Dmax and Dmin of each of cyan, magenta, and yellow at the gray portion are shown in [Table 6].

/29

[Table 6]

Light-sensitive materials	Dmax			Dmin		
	Cyan	Magenta	Yellow	Cyan	Magenta	Yellow
201	2.15	2.21	2.10	0.22	0.23	0.24
202	2.13	2.20	2.09	0.17	0.15	0.16
203	2.16	2.22	2.10	0.16	0.15	0.15
204	2.15	2.17	2.08	0.16	0.16	0.15
205	2.16	2.21	2.09	0.17	0.15	0.15
206	2.14	2.19	2.09	0.16	0.16	0.16
207	2.17	2.18	2.11	0.16	0.15	0.15

By contrast to the light-sensitive material 201, the amount of stains was found to be reduced in the light-sensitive materials 202 to 207 to which the compounds according to the present invention had been added.

Applicant: Fuji Photo Film Co., Ltd.

Amendment of Proceedings

12/13/1988

Commissioner:

1. Identification of the Case: Japanese Patent No. 200604 (1988)

2. Title of the Invention: Heat-developable color photographic
light-sensitive material

3. Person Filing Amendment

Relationship to case: Applicant

Address: 210 Nakanuma, Minamiashigara, Kanagawa

Name: (520) Fuji Photo Film Co., Ltd.

Representative, Minoru Onishi

Address: 2-26-30, Nishiazabu, Minato-ku, Tokyo, 106.

Fuji Photo Film Co., Ltd. Tokyo Head Office

Tel: (406) 2537

4. Object for Amendment :[Detailed Description of the Invention]
in Specification

5. Contents of Amendment

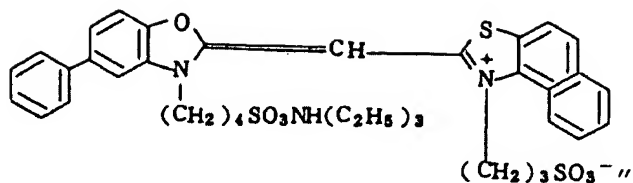
The descriptions in [Detailed Description of the Invention]
in Specification are amended as follows:

1) Amendment:

"coupler print" in Page 3, Line 13
into "color print".

2) Insert:

"Sensitizing dye (d)



after the last line of page 88.

/30

3) Delete:

"Sensitizing dye (1)* 1.07×10^{-3} " in the table in page 101.

END

Amendment of Proceedings (system)

(illegible)/19/1988

Commissioner:

1. Identification of the Case: Japanese Patent No. 200604 (1988)

2. Title of the Invention: Heat-developable color photographic light-sensitive material

3. Person Filing Amendment

Relationship to case: Applicant

Address: 210 Nakanuma, Minamiashigara, Kanagawa

Name: (520) Fuji Photo Film Co., Ltd.

Representative, Minoru Onishi

Address: 2-26-30, Nishiazabu, Minato-ku, Tokyo, 106.

Fuji Photo Film Co., Ltd. Tokyo Head Office

Tel: (406) 2537

4. Date of Amendment Directive

11/29/1988 (date of mailing)

5. Object for Amendment: Specification, pages 19 to 35, 37 to 41 and 49 to 78.

6. Contents of Amendment

Amendment is described in the sheet attached.

(Continued from the previous page) it is preferred that the electron transferring agent is present in the silver halide emulsion layer. In the present invention, at least two sets of such light-sensitive layers are used. In order to reproduce full colors, three sets of light-sensitive layers each having a different color sensitivity are generally used. Known examples of the combination include a combination of a blue-sensitive layer, a green-sensitive layer and a red-sensitive layer, and a combination of a green-sensitive layer, a red-sensitive layer and an infrared-sensitive layer. These light-sensitive layers can be disposed in various disposition orders as known from conventional color photographic light-sensitive materials. In addition, as needed, each light-sensitive layer can also be composed of two or more layers.

Next, the reducible dye-providing compounds that can be used in the present invention are described in the following.

The reducible dye-providing compound used in the present invention is preferably a compound represented by the following formula (C-I):



wherein PWR represents a group which releases $-(\text{Time})_t\text{-Dye}$ by being reduced.

Time represents a group which releases Dye through a

/31

subsequent reaction after being released from PWR as $-(\text{Time})_t\text{-Dye}$.

t represents an integer of 0 to 1.

Dye represents a dye or a precursor thereof.

First, PWR is described in greater detail.

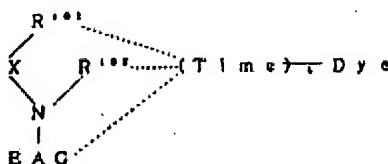
PWR can be a group corresponding to a moiety containing the electron acceptive center and the intramolecular nucleophilic substitution reaction center in a compound capable of releasing a photographic reagent by an intramolecular nucleophilic substitution reaction after being reduced as disclosed in U.S. Patent. No. 4,139,389, U.S. Patent. No. 4,139,379 and U.S. Patent. No. 4,564,577, Japanese Unexamined Patent Publication No. S59-185333 and Japanese Unexamined Patent Publication No. S57-84453, or can be a group corresponding to a moiety containing the electron acceptive quinoid center and the carbon atom bonding the quinoid center to a photographic reagent in a compound capable of releasing the photographic reagent by an

intramolecular electron transfer reaction after being reduced as disclosed in U.S. Patent No. 4,232,107, Japanese Unexamined Patent Publication No. S59-101649, Research Disclosure (1984) IV, 24025, and Japanese Unexamined Patent Publication No. S61-88257. Further, PWR can be a group corresponding to a moiety containing the aryl group substituted by an electron attractive group and the atom (a sulfur atom, a carbon atom, or a nitrogen atom) bonding the aryl group to a photographic reagent in a compound capable of releasing the photographic reagent by the cleavage of a single bond after being reduced as disclosed in Japanese Unexamined Patent Publication No. S56-142530, U.S. Patent No. 4,343,893 and U.S. Patent No. 4,619,884. Further, it can be a group corresponding to a moiety containing the nitro group and the carbon atom bonding the nitro group to a photographic reagent in a nitro compound capable of releasing the photographic reagent after receiving electrons as disclosed in U.S. Patent. No. 4,450,223, or can also be a group corresponding to a moiety containing the geminaldinitro moiety and the carbon atom bonding the geminaldinitro [amended typo in "geminaldinitro"] moiety to a photographic reagent in a dinitro compound capable of releasing the photographic reagent by a β -elimination reaction after receiving electrons as disclosed in U.S. Patent. No. 4,609,610.

Further, examples of compounds as PWR include: a compound having a SO₂-X (wherein X represents an oxygen atom, a sulfur atom or a nitrogen atom) and an electron attractive group in the molecule as disclosed in Japanese Patent Application No. S62-106885; a compound having a PO-X bond (wherein X is the same as above) and an electron attractive group in the molecule as disclosed in Japanese Patent Application No. S62-106895; and a compound having a C-X' bond (wherein X' is the same as X or represents -SO₂-) and an electron attractive group in the molecule as disclosed in Japanese Patent Application No. S62-106887.

In order to more sufficiently achieve the object of the present invention, of the compounds represented by general formula [C-I], those which can be represented by general formula [C-II] are preferred.

General Formula [C-II]



(Time)_tDye is bonded to at least one of R¹⁰¹, R¹⁰², and EAG.

The moiety corresponding to PWR of general formula [C-II] is described.

X represents an oxygen atom (-O-), a sulfur atom (-S-) or a nitrogen-containing group (-N(R¹⁰³)-).

R^{101} , R^{102} , and R^{103} each represents a group besides a hydrogen atom or a simple bond.

Examples of the groups besides a hydrogen atom represented by R^{101} , R^{102} , and R^{103} include an alkyl group, an aralkyl group, an alkenyl group, an alkynyl group, an aryl group, a heterocyclic group, a sulfonyl group, a carbamoyl group and a sulfamoyl group, and these groups can have a substituent.

R^{101} and R^{103} each preferably represents an alkyl group, an alkenyl group, an alkynyl group, an aryl group, a heterocyclic group, an acyl group or a sulfonyl group, each of which can be substituted or unsubstituted. The carbon number of each group represented by R^{101} and R^{103} is preferably 1 to 40.

R^{102} preferably represents a substituted or unsubstituted acyl group or sulfonyl group. Examples of the acyl group and sulfonyl group include the same as described in R^{101} and R^{103} . The carbon number is preferably 1 to 40.

R^{101} , R^{102} and R^{103} may be combined with each other to form a 5- to 8-membered ring.

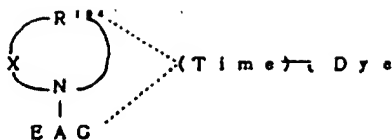
X is particularly preferably an enzyme.

EAG will be described later.

/32

In order to achieve the object of the present invention, of the compounds represented by general formula [C-II], compounds represented by general formula [C-III] are preferred:

General Formula [C-III]



(Time)_tDye is bonded to at least either R¹⁰⁴ or EAG.

X is the same as described above.

R¹⁰⁴ represents an atomic group forming a 5- to 8-membered monocyclic or condensed heterocyclic ring containing the nitrogen atom by combining with X and the nitrogen atom.

EAG represents a group capable of accepting an electron from a reducing substance and is bonded to the nitrogen atom. EAG is preferably a group represented by the following general formula [A]:

General Formula [A]

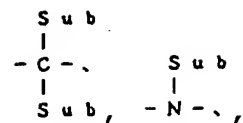


In general formula [A],

Z₁ represents $\begin{array}{c} | \\ -C- \\ | \end{array}$ s u b or $\begin{array}{c} | \\ -N- \end{array}$.

V_n represents an atomic group forming a 3- to 8-membered aromatic group with Z₁ and Z₂, and n represents an integer of 3 to 8.

V₃ represents -Z₃-, V₄ represents -Z₃-Z₄-, V₅ represents -Z₃-Z₄-Z₅-, V₆ represents -Z₃-Z₄-Z₅-Z₆-, V₇ represents -Z₃-Z₄-Z₅-Z₆-Z₇-, and V₈ represents -Z₃-Z₄-Z₅-Z₆-Z₇-Z₈-.



In the above formulae, Z_2 to Z_8 each represents -O-, -S- or -SO₂-, and Sub represents a simple bond (π -bond), a hydrogen atom or the substituent shown below. The Subs can be the same or different, and may combine with each other to form a 3- to 8-membered saturated or unsaturated carbon ring or heterocyclic ring.

In general formula [A], Subs are selected such that the total sum of the Hammett's substituent constants σ -para of the substituents is preferably +0.50 or more, is more preferably +0.70 or more, and is most preferably +0.85 or more.

The EAG is preferably an aryl group or heterocyclic group substituted by at least one electron attractive group. The substituents bonded to the aryl group or the heterocyclic group of EAG can be used for controlling the properties of the whole compound. Examples of the properties of the whole compound include the acceptability of electrons as well as the water-solubility, the oil-solubility, the diffusibility, the sublimability, the melting point, the dispersibility for a binder such as gelatin or the like, the reactivity for a nucleophilic group and the reactivity for an electrophilic group.

Specific examples of EAG are described in European Patent No. 220746A2, pages 6 to 7.

Time represents a group capable of releasing Dye via the subsequent reaction by the cleavage of a nitrogen-oxygen bond, a nitrogen-nitrogen bond or a nitrogen-sulfur bond as a trigger.

Various groups that can be represented by Time are known; known examples of such groups include those described in Japanese Unexamined Patent Publication No. S61-147244, pages 5 and 6, Japanese Unexamined Patent Publication No. S61-236549, pages 8 to 14, and Japanese Patent Application No. S61-88625, pages 36 to 44.

Known examples of the dyes represented by Dye include azo dyes, azomethine dyes, anthraquinone dyes, naphthoquinone dyes, styryl dyes, nitro dyes, quinoline dyes, carbonyl dyes and phthalocyanine dyes. Further, these dyes can be used in the form of being temporarily shifted to a shorter wavelength side, which can be recolored on development.

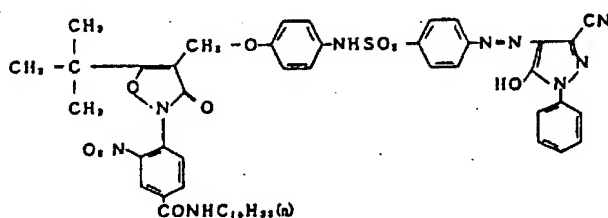
Specific examples of the Dyes include those disclosed in European Patent No. 76,492A and Japanese Unexamined Patent Publication No. S59-165054.

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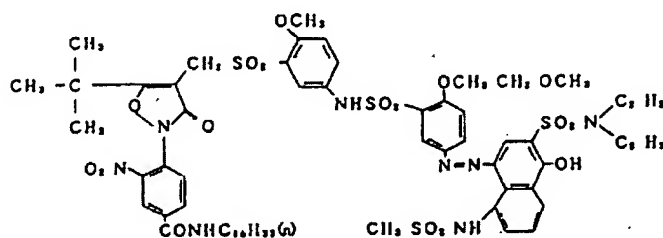
It is necessary that the compound represented by the above general formula [C-II] or [C III] is immobile in a photographic layer; therefore, it is preferred that the compound has a ballast group having 8 or more carbon atoms at the position of EAG, R^{101} , R^{102} , R^{104} or X (in particular, at the position of EAG).

Typical examples of the reducible dye-providing compound used in the present invention are specifically listed below, but these examples do not restrict the present invention in any way but the reducible dye-providing compound described, for example, in European Patent No. 220746A2 and Published Technical Report No. 87-6199 can also be used in the present invention.

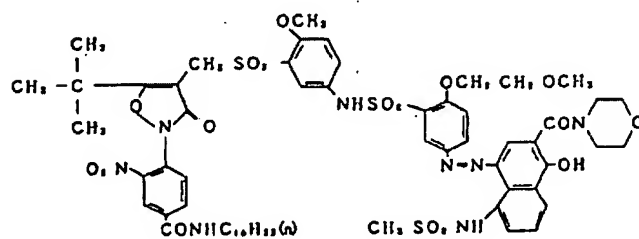
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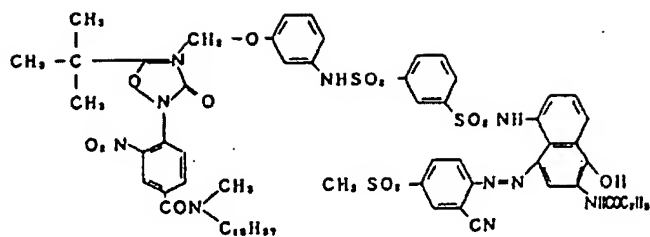
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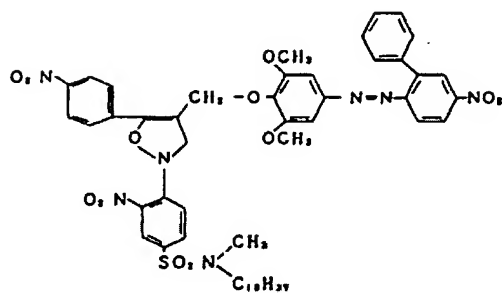
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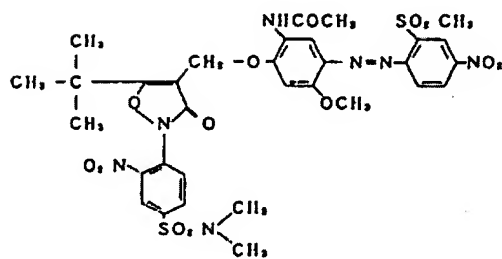
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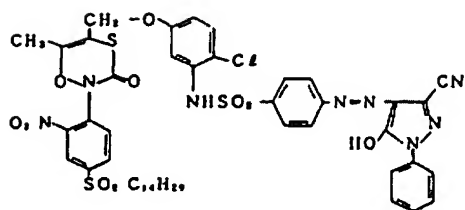


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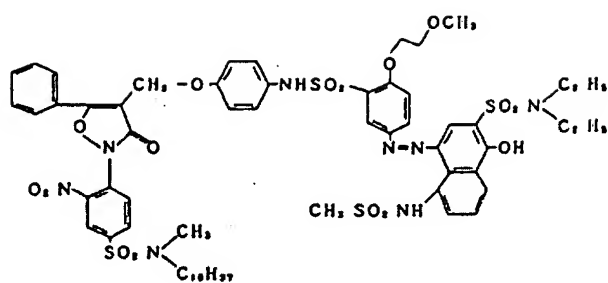


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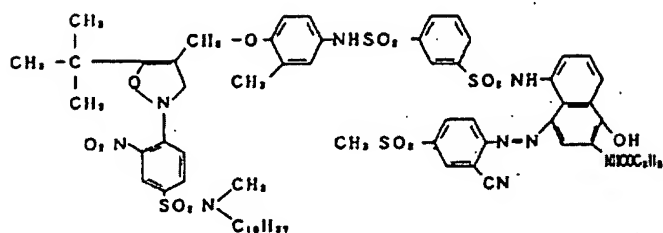
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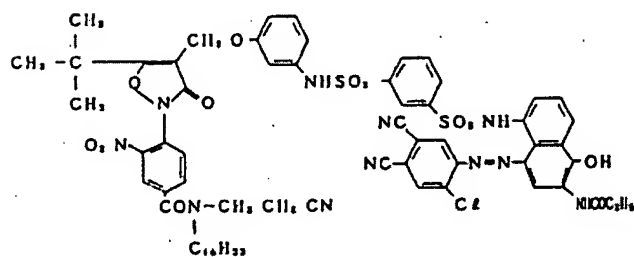
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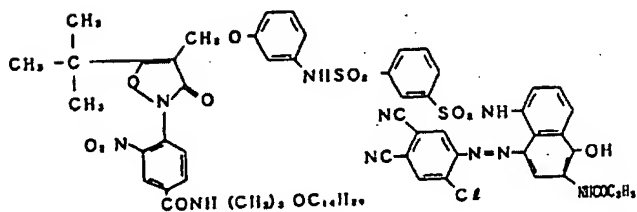
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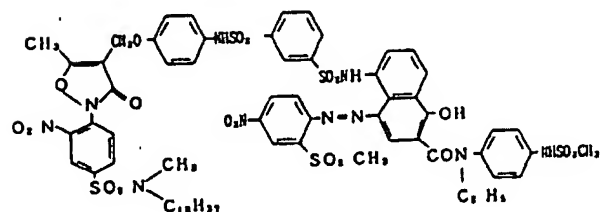
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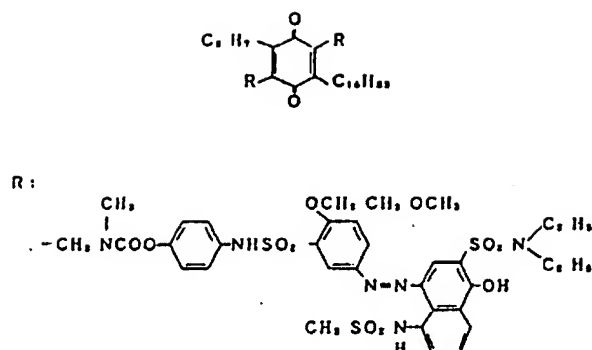
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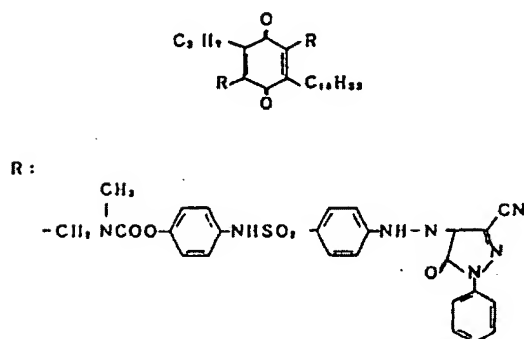
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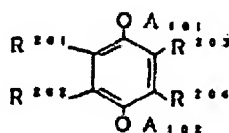
These compounds can be synthesized by the methods described in the above-mentioned patent specifications.

The amount of the dye-providing compound may vary depending on the extinction coefficient of the dye, but is usually in a range of from 0.05 to 5 mmol/m², and is preferably in a range of from 0.1 to 3 mmol/m². The dye-providing compounds can be used alone or in combination of two or more. Further, in order to obtain black images or images composed of different colors, two or more types of dye-providing compounds each releasing a mobile

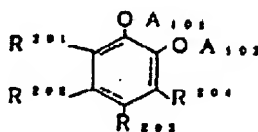
dye each having a different color can be used as a mixture thereof in such a way that a mixture of, for example, at least one type of a cyan dye-providing compound, at least one type of a magenta dye-providing compound and at least one type of a yellow dye-providing compound is incorporated into a layer containing silver halide or a layer adjacent to the silver halide-containing layer as described in Japanese Unexamined Patent Publication No. S60-162251.

In the present invention, an electron donor and an electron transferring agent (ETA) are used, the details of which are described in European Patent No. 220746A2 and Published Technical Report 87-6199. Particularly preferred electron donors (and the precursors thereof) are the compounds represented by following general formula [C] or [D]:

General Formula [C]



General Formula [D]



wherein A₁₀₁ and A₁₀₂ each represents a hydrogen atom or a protective group for a phenolic hydroxyl group, said protective group being releasable by a nucleophilic reagent.

In this case, examples of the nucleophilic reagent include anionic reagents, such as $\text{OH}^{(-)}$, $\text{RO}^{(-)}$ (wherein R represents an alkyl group, an aryl group or the like) and hydroxamic acid anions $\text{SO}_3^{2(-)}$, and compounds having a non-covalent electron pair, such as primary or secondary amines, hydrazines, hydroxylamines, alcohols and thiols.

Preferred examples of A_{101} and A_{102} include a hydrogen atom, an acyl group, an alkylsulfonyl group, an arylsulfonyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a dialkylphosphoryl group, a diarylphosphoryl group, and the protective groups disclosed in Japanese Unexamined Patent Publication No. S59-197037 and Japanese Unexamined Patent Publication No. S59-20105 and, if possible, A_{101} and A_{102} may combine with R^{201} , R^{202} , R^{203} and R^{204} to form a ring. In addition, A_{101} and A_{102} can be the same or different from each other.

R^{201} , R^{202} , R^{203} and R^{204} each represents a hydrogen atom, an alkyl group, an aryl group, an alkylthio group, an arylthio group, a sulfonyl group, a sulfo group, a halogen atom, a cyano group, a carbamoyl group, a sulfamoyl group, an amido group, an imido group, a carboxyl group, a sulfonamido group or the like. These groups can, if possible, have a substituent.

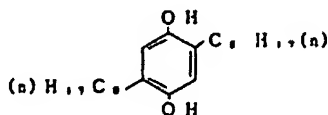
In addition, the sum of the carbon atoms of the groups represented by R^{201} , R^{202} , R^{203} and R^{204} is 8 or more. Further, in general formula [C], R^{201} and R^{202} and/or R^{203} and R^{204} may combine

with each other to form a saturated or unsaturated ring, and in general formula [D], R^{201} and R^{202} , R^{202} and R^{203} , and/or R^{203} and R^{204} may combine with each other to form a saturated or unsaturated ring.

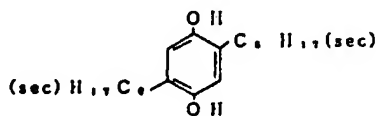
In the electron donors represented by the above general formula [C] or [D], it is preferred that at least two of R^{201} to R^{204} are substituents besides a hydrogen atom. Compounds in which at least one of R^{201} and R^{202} and at least one of R^{203} and R^{204} are substituents besides hydrogen atom are particularly preferred.

The electron donors can be used in a combination thereof, and the electron donor can also be used together with the precursor thereof. Further, the electron donor can be the same compound as the reducing substances used in the present invention. Specific examples of the electron donor are listed below, but this is not an exhaustive list.

(ED-1)

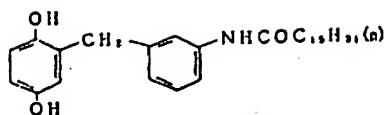


(ED-2)

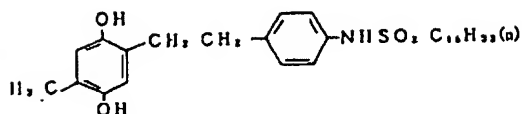


/36

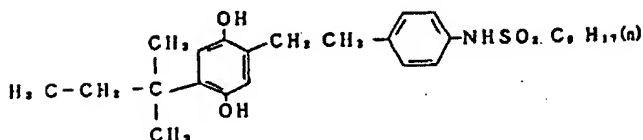
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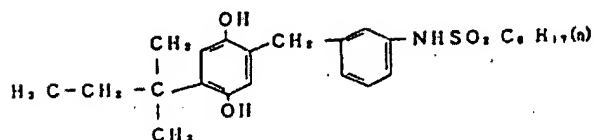
(ED-4)



(ED-5)



(ED-6)



The ETA precursor used in the present invention is a compound which does not have a developing action during the preservation of the light-sensitive material before use but finally releases the ETA by the action of an appropriate activator [corrected typo "activator"] (e.g., a base and a nucleophilic agent) or the action of heat.

In particular, the ETA precursor used in the present invention does not have a function as an ETA before development because the reactive functional group of the ETA is blocked by a blocking group but functions as an ETA under an alkaline

condition or by heating because in this case, the blocking group is cleaved.

Examples of the ETA precursor used in the present invention include 1-phenyl-3-pyrazolidinone-2- or 3-acyl derivatives, 2-aminoalkyl or hydroxyalkyl derivatives, metal salts (e.g., lead salts, cadmium salts, calcium salts and barium salts) of hydroquinone, catechol or the like, halogenated acyl derivatives of hydroquinone, oxazine or bisoxazine derivatives of hydroquinone, lactone-type ETA precursors, hydroquinone precursors having a quaternary ammonium group, cyclohex-2-ene-1,4-dione type compounds, compounds releasing an ETA by an electron transfer reaction, compounds releasing an ETA by an intramolecular nucleophilic substitution reaction, ETA precursors blocked by a phthalide group, and ETA precursors blocked by an indomethyl group.

The ETA precursors used in the present invention are known compounds; known examples include the developer precursors described in U.S. Patent. Nos. 3,767,704, 3,241,967, 3,246,988, 3,295,978, 3,462,266, 3,586,506, 3,615,439, 3,650,749, 4,209,580, 4,330,617 and 4,310,612, British Patent Nos. 1,023,701, 1,231,830, 1,258,924, and 1,346,920, Japanese Unexamined Patent Publication Nos. S57-40245, S58-1139, S58-1140, S59-178458, S59-182449 and S59-182450.

In particular, the precursors of 1-phenyl-3-pyrasolidinones described in Japanese Unexamined Patent Publication Nos. S59-178458, S59-182449 and S59-182450 are preferred.

The ETA can be used together with the ETA precursor.

In the present invention, the combination of the electron donor and the ETA is preferably incorporated into the heat-developable color photographic light-sensitive material. Further, the electron donors and ETAs or the precursors of thereof each can be used as a combination of two or more, and they can be added to each of the emulsion layers (e.g., a blue-sensitive emulsion layer, a green-sensitive emulsion layer, a red-sensitive emulsion layer, an infrared-sensitive emulsion layer, and an ultraviolet-sensitive emulsion layer) of the light-sensitive material, can also be added to specific emulsion layers only, can also be added to a layer adjacent to the emulsion layer (e.g., an anti-halation layer, a subbing layer, an interlayer, and a protective layer), or can also be added to all the layers. The electron donor and ETA can be added to the same layer or can be added separately to separate layers. Further, these reducing agents and the dye-providing compound can be added to the same layer or can be added separately to separate layers, but it is preferred that the non-diffusible electron donor is present in the layer containing the dye-providing compound.

The ETA can be incorporated in an image-receiving material (dye-fixing layer) and, when a slight amount of water exists on heat development, the ETA can be dissolved in the water. The preferred amounts of the electron donor and ETA or the precursors thereof are, as the total amounts, 0.01 to 50 mol, preferably 0.1 to 5 mol, as against 1 mol of the dye-providing compound, and are 0.001 to 5 mol, preferably 0.01 to 1.5 mol, as against 1 mol of the silver halide.

Further, the amount of the ETA is 60 mol% or less, and is more preferably 40 mol% or less of the whole amount of the reducing agents. When the ETA is supplied as a solution dissolved in water during processing, the ETA concentration is preferably 10^{-4} mol/L to 1 mol/L.

In order to introduce the reducing substance, the dye-providing compound, the electron donor, the electron transfer agent or the precursors thereof, and other hydrophobic additives into a hydrophilic colloid layer, a high-boiling organic solvent can be used, known examples of which include phthalic acid alkyl esters (e.g., dibutyl phthalate and dioctyl phthalate), phosphoric acid esters (e.g., diphenyl phosphate, triphenyl phosphate, tricyclohexyl phosphate, tricresyl phosphate, and dioctylbutyl phosphate), citric acid esters (e.g., tributyl acetyl-citrate), benzoic acid esters (e.g., octyl benzoate),

alkylamides (e.g., diethyl laurylamide), fatty acid esters (e.g., dibutoxy succinate and dioctyl azelate), trimesinic acid esters (e.g., tributyl trimesinate), the carboxylic acids described in Japanese Patent Application No. S61-231500, and the compounds described in Japanese Unexamined Patent Publication No. S59-83154, S59-178451, S59-178452, S59-178453, S59-178454, S59-178455 and S59-178457; in such cases, the method described in U.S. Patent. No. 2,322,027 can be applied or the above-mentioned materials can be dissolved in an organic solvent having a boiling point of from approximately 30 to 160 degrees Celsius, such as lower alkyl acetates, such as ethyl acetate and butyl acetate, ethyl propionate, secondary butyl alcohol, methyl isobutyl ketone, β -ethoxy ethyl acetate, methylcellosolve acetate, and cyclohexanone, thereby being decomposed to hydrophilic colloid. A mixture of the above-mentioned high-boiling organic solvent and low-boiling organic solvent can be used. Further, after dispersion, as needed, the low-boiling organic solvent can be removed by ultra-filtration or the like. The amount of the high-boiling organic solvent used is 10 g or less, preferably 5 g or less, as against 1 g of the dye-providing compound used. The amount of the high-boiling organic solvent used is 5 g or less, preferably 2 g or less, as against 1 g of the non-diffusible reducing agent. The amount of the high-boiling organic solvent used is 1 g or less, preferably 0.5

g or less, and more preferably 0.3 g or less, as against 1 g of the binder used. The dispersion method by a polymer as described in Japanese Examined Patent Publication No. S51-39853 and Japanese Unexamined Patent Publication No. S51-59943. In addition, the above-mentioned materials can also be directly dispersed in an emulsion, or after dissolving them in water or an alcohol, the resulting solution can be dispersed in a gelatin or an emulsion.

When the compounds are substantially insoluble in water, the compounds can alternatively be dispersed in a binder as fine particles. (e.g., methods as described in Japanese Unexamined Patent Nos. S59-174830 and S53-102733 and Japanese Patent Application No. 62-106882).

In the case of dispersing hydrophobic substances in a hydrophilic colloid, various surfactants can be used; known examples of surfactants that can be used in this case include those described in Japanese Examined Patent Publication No. S59-157636, pages 37 and 38.

The inventive heat-developable light-sensitive material has a fundamentally light-sensitive silver halide, a binder, an electron donor, an electron transferring agent and a reducible dye-providing compound on a substrate and, as needed, the inventive light-sensitive material can further contain an organic metal salt oxidizing agent. These components usually

added to the same layer but can also be separately added to separate layers in the case where the components can be reacted with each other. For example, when the colored dye-providing compound is present in a layer under a silver halide emulsion layer, the reduction of the sensitivity can be prevented. The reducing agent can be preferably incorporated into the heat-developable light-sensitive material but can be provided externally, for example, by a method wherein the reducing agent is diffused into the light-sensitive material from a dye-fixing material as will be described below.

In order to obtain a wide range of colors in the

/38

chromaticity diagram by using three primary colors of yellow, magenta, and cyan, a combination of at least three silver halide emulsion layers each having light sensitivity in a different spectral region can be used. Examples of the combinations of three sensitive layers that can be applied include a combination of a blue-sensitive layer, a green-sensitive layer, and a red-sensitive layer, and a combination of a green-sensitive layer, a red-sensitive layer, and an infrared-sensitive emulsion layer. The light-sensitive layers can be disposed in various disposition orders conventionally employed for ordinary color photographic light-sensitive materials. Further, each light-sensitive layer can be optionally composed of two or more layers.

The inventive heat-developable light-sensitive material can be provided with various subsidiary layers, such as a protective layer, a subbing layer, an intermediate layer, a yellow filter layer, an anti-halation layer and a back layer.

The silver halide used in the present invention can be any of silver chloride, silver bromide, silver iodobromide, silver chlorobromide, silver chloriodide, and silver chloriodobromide.

The silver halide emulsion used in the present invention can be a surface latent image-type emulsion. The term "surface latent image-type emulsion" refers to an emulsion in which latent images are formed on the particle surface and is also referred to "negative emulsion". The definition of the surface latent image-type emulsion is described in Japanese Examined Patent Publication No. S58-9410.

The silver halide emulsion used in the present invention can also be a so-called core/shell-type emulsion wherein the inside of the particles has a different phase from the particle surface layer. The silver halide emulsion can be either a monodisperse silver halide emulsion or a polydisperse silver halide emulsion, and can also be a mixture of monodisperse silver halide emulsions. The particle size of the silver halide particles used in the present invention is preferably 0.1 to 2 μ , and is particularly preferably 0.2 to 1.5 μ . The crystal habit

of the silver halide particles can be cubic, octahedral, tetradecahedral, tabular of a high aspect ratio, and the like.

Examples of silver halide emulsions used in the present invention include any of the silver halide emulsions described in U.S. Patent. No. 4,500,626, column 50, U.S. Patent. No. 4,628,021, Research Disclosure ("RD", hereinafter), No. 17029 (1978), and Japanese Unexamined Patent Publication No. S62-253159.

The silver halide emulsion can be used as a primitive emulsion, but is usually chemically sensitized before use. In this case, a sulfur sensitization method, a reduction sensitization method and a noble metal sensitization method, which are known for conventional photographic light-sensitive materials, can be applied alone or in a combination thereof. These chemical sensitizations can be carried out in the presence of a nitrogen-containing heterocyclic compound (as disclosed in Japanese Unexamined Patent Publication No. S62-253159).

The coating amount of the light-sensitive silver halide used in the present invention is in a range of from 1 mg to 10 g/m² on the silver basis.

In the present invention, an organic metal salt can be used as an oxidizing agent together with the light-sensitive silver halide. Of organic metal salts, an organic silver salt can be particularly preferably used.

Examples of organic compounds that can be used to form the above-mentioned organic silver salt oxidizing agents include benzotriazoles, fatty acids and other compounds described in U.S. Patent. No. 4,500,626, columns 52 to 53. Known examples of organic compounds further include silver salts of carboxylic acids having an alkyl group, such as phenyl propiolic acid silver, described in Japanese Unexamined Patent Publication No. S60-113235 and acetylene silver described in Japanese Unexamined Patent Publication No. S61-249044. These organic silver salts can be used in combination of two or more.

The above-mentioned organic silver salt can be used in an amount of from 0.01 to 10 mol, preferably from 0.01 to 1 mol, as against 1 mol of the light-sensitive silver halide. The suitable total coating amount of the light-sensitive silver halide and the organic silver salt is from 50 mg to 10 g/m² on the silver basis.

In the present invention, various antifoggants or photographic stabilizers can be used. Examples of such agents include azoles and azaindenes described in RD, No. 17643, pages 24 to 25 (1978), nitrogen-containing carboxylic acids and phosphoric acids described in Japanese Unexamined Patent Publication No. S59-168442, mercapto compounds and the metal salts thereof described in Japanese Unexamined Patent

Publication No. S59-111636, and acetylene compounds described in Japanese Unexamined Patent Publication No. S62-87957.

The silver halide used in the present invention can be spectrally sensitized by methine dyes and the like. Examples of such dyes for the spectral sensitization include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes, and hemioxonol dyes.

Specific examples of the sensitizing dyes include those described in U.S. Patent. No, 4,617,257,

/39

Japanese Unexamined Patent Nos. S59-180550 and S60-140335, and RD, No. 17029, pages 12 to 13 (1978).

These sensitizing dyes can be used alone or in combination thereof, and a combination of sensitizing dyes is frequently used for the purpose of supersensitization.

In addition to sensitizing dyes, a dye which has no spectral sensitizing action by itself or a compound which does not substantially absorb visible light but shows a supersensitization can be contained in the emulsion (see, for example, those described in U.S. Patent. No. 3,615,641 and Japanese Patent Application S61-226294).

The timing for adding these sensitizing dyes to the emulsion can be before or after the chemical ripening, or before

or after the nucleus formation of the silver halide particles according to U.S. Patent Nos. 4,183,756 and 4,225,666. The addition amount of the sensitizing dye is from approximately 1×10^{-8} to 1×10^{-2} mol as against 1 mol of the silver halide.

Hydrophilic binders can be preferably used as a binder for layers constituting the light-sensitive material and dye-fixing material. Examples of such hydrophilic binders include those described in Japanese Unexamined Patent Publication No. S62-253159, pages 26 to 28. More specifically, a transparent or opaque hydrophilic binder can be preferably used, known examples of which include: natural compounds including proteins, such as gelatin and gelatin derivatives, protein or cellulose derivatives, and polysaccharides, such as starch, gum Arabic, dextran, and pluran; and synthetic high molecular compounds, such as polyvinyl alcohol, polyvinylpyrrolidone and acrylamide polymers. Examples of the binders further include high water-absorptive polymers described in Japanese Unexamined Patent Publication No. S62-245260, i.e., a homopolymer of a vinyl monomer having $-\text{COOM}$ or $-\text{SO}_3\text{M}$ (wherein M represents a hydrogen atom or an alkali metal) and a copolymer of the above vinyl monomers or of the above vinyl monomer and other vinyl monomers (e.g., sodium methacrylate, ammonium methacrylate, and Sumika Gel L-5H, manufactured by Sumitomo Chemical Co., Ltd.). These binders can be used in combination of two or more.

In the case of employing a system of carrying out heat-development by supplying a slight amount of water, the absorption of water can be rapidly conducted by using the above-mentioned high water-absorptive polymer. Further, when the high water-absorptive polymer is used in the dye-fixing layer or a protective layer, the retransfer of dyes from a dye-fixing material to other materials upon completion of the transferring can be prevented.

In the present invention, the coating amount of the binder is preferably 20 g or less, more preferably 10 g or less, and particularly preferably 7 g or less, as against 1 m² of the light sensitive material.

In the layers (including a back layer) constituting the light-sensitive material or the dye-fixing material, various polymer latexes can be contained for the purpose of improving the film properties, such as the dimensional stability, preventing curling, preventing sticking, preventing cracking of layers, and the prevention of the occurrence of pressure sensitization or desensitization. Specific examples of such polymer latexes include any of those described in Japanese Unexamined Patent Publication Nos. S62-245258, S62-136648 and S62-110066. In particular, when a polymer latex having a low glass transition point (40 degrees Celsius or less) is used in a mordant layer, the occurrence of cracking of the mordant layer

can be prevented and, when a polymer latex having a high glass transition point is used in a back layer, the curling preventing effect can be obtained.

In this invention, a compound capable of activating the development of, and also stabilizing, the images formed can be used in the light-sensitive material. Preferred examples of such compounds are described in U.S. Patent. No. 4,500,626, columns 51 to 52.

In the system which forms images by the diffusion transfer of dyes, dye-fixing material is used together with the light-sensitive material. The dye-fixing material and the light-sensitive material can be separately [corrected typo "separately"] formed on different substrates or can also be formed on the same substrate. The relationship between the light-sensitive material and the dye-fixing material, the relationship between the above materials and substrates, and the relationship between the above materials and a white reflecting layer which are described in U.S. Patent. No. 4,500,626, column 57 can also be applied to the present invention.

The dye-fixing material which can be preferably used in the present invention has at least one layer containing a mordant and a binder. Mordants which are known in the field of photography can be used in the present invention. Specific

examples of such mordants include those described in U.S. Patent. No. 4,500,626, columns 58 to 59

/40

and Japanese Unexamined Patent Publication No. S61-88256, pages 32 to 41, and those described in Japanese Unexamined Patent Publication Nos. S62-244043 and S62-244036. Further, the dye-acceptive high molecular compounds as described in U.S. Patent. No. 4,463,079 can also be used in the present invention.

The dye-fixing material can optionally have an auxiliary layer, such as a protective layer, a releasing layer and a curling prevention layer, with the formation of a protective layer being effective.

The layers constituting the light-sensitive material and the dye fixing material can contain a plasticizer, a slipping agent and a high-boiling organic solvent as a release-property improving agent for the dye-fixing material from the light-sensitive material. Specific examples of such agents include those described in Japanese Unexamined Patent Publication No. S62-253159, page 25 and Japanese Unexamined Patent Publication No. S62-245253.

Further, in order to achieve the above object, various silicone oils (including any silicone oils from dimethylsilicone oil to other modified silicone oils obtained by introducing various organic groups to dimethyl siloxane) can be used.

Examples of such silicone oils include various modified silicone oils described in "Modified Silicone Oil", Technical Material P6-18B, published by Shin-Etsu Silicone K. K., with carboxymodified silicone (trade name, X-22-3710) being particularly preferred.

Further, the silicone oils described in Japanese Unexamined Patent Publication No. S62-215953 and Japanese Patent Application No. S62-23687 can be effectively used.

The light-sensitive material and the dye-fixing material can contain a discoloration inhibitor. Examples of such a discoloration inhibitor include antioxidants, ultraviolet absorbents and specific types of metal complexes.

Examples of the antioxidants include chroman compounds, coumaran compounds, phenol compounds (e.g., hindered phenols), hydroquinone derivatives, hindered amine derivatives and spiroindane compounds. The compounds described in Japanese Unexamined Patent Publication No. S61-159644 can also be effectively used.

Examples of the ultraviolet absorbents include benzotriazole compounds (e.g., those described in U.S. Patent. No. 3,533,794), 4-thiazolidone compounds (e.g., those described in U.S. Patent. No. 3,352,681), benzophenone compounds (e.g., those described in Japanese Unexamined Patent Publication No. S46-2784), and the compounds described in Japanese Unexamined

Patent Publication No. S54-48535, Japanese Unexamined Patent Publication No. S62-136641 and Japanese Unexamined Patent Publication No. S61-88256. Further, the ultraviolet absorptive polymers described in Japanese Unexamined Patent Publication No. S62-260152 can also be effectively used.

Examples of the metal complexes include the compounds described in U.S. Patent. No. 4,241,155, U.S. Patent No. 4,245,018, columns 3 to 36, U.S. Patent No. 4,254,195, columns 3 to 8, Japanese Unexamined Patent Publication No. S62-174741, Japanese Unexamined Patent Publication No. S61-88256, pages 27 to 29, Japanese Patent Application No. 62-234103, Japanese Patent Application No. S62-31096 and Japanese Patent Application No. S62-23059.

Examples of effective discoloration inhibitors are described in Japanese Unexamined Patent Publication No. S62-215272, pages 125 to 137.

The discoloration inhibitors which inhibit the dyes transferred to the dye-fixing material can be contained in the dye-fixing material, or can also be provided externally, for example, from the light-sensitive material.

The above-mentioned antioxidants, ultraviolet absorbents and metal complexes can be used in combination.

Brightening agents can be used in the light-sensitive material and the dye-fixing material. In particular, it is

preferred that the brightening agent is incorporated into the dye-fixing material or is provided externally, for example, from the light-sensitive material. Examples of such brightening agents include compounds described in K. Veenkataraman, "the Chemistry of Synthetic Dyes", Vol. V, Chapter 8, and Japanese Unexamined Patent Publication No. S61-143752. Specific examples of the compounds include stilbene compounds, coumarin compounds, biphenyl compounds, benzoxazolyl compounds, naphthalimide compounds, pyrazolidone compounds and carbostyryl compounds.

The brightening agent can be used in combination with a discoloration inhibitor.

Examples of hardening agents that can be used in the layers constituting the light-sensitive material and the dye-fixing material include those described in U.S. Patent. No. 4,678,739, column 41, Japanese Unexamined Patent Publication No. S59-116655, Japanese Unexamined Patent Publication No. S62-245261 and Japanese Unexamined Patent Publication No. S61-18942.

/41

Specific examples of the hardening agents include aldehyde hardening agents (e.g., formaldehyde), aziridine hardening agents, epoxy series hardening agents (e.g.,

$\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-(\text{CH}_2)_n-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2$), vinylsulfone hardening agents [e.g.,

N,N'-ethylene-bis(vinylsulfonylacetamido)ethane], N-methylol hardening agents (e.g., dimethylolurea) and high molecular

hardening agents (e.g., the compounds described in Japanese Unexamined Patent Publication No. S62-234157).

The layers constituting the light-sensitive material or the dye fixing material can contain various surfactants as coating aids and in order to improve the releasability and slipping properties, provide the antistatic properties and accelerate the development. Specific examples of surfactants are described in Japanese Unexamined Patent Publication No. S62-173463 and Japanese Unexamined Patent Publication No. S62-183457.

The layers constituting the light-sensitive material and the dye-fixing material can contain an organic fluoro compound in order to improve the slipping properties, providing the antistatic properties and improve the releasability. Typical examples of organic fluoro compounds the fluorine surfactants described in Japanese Examined Patent Publication No. S57-9053, columns 8 to 17, Japanese Unexamined Patent Publication No. S61-20944 and Japanese Unexamined Patent Publication No. S62-135826, and hydrophobic fluorine compounds, such as oily fluorine compounds, such as fluorine oil, and solid fluorine compound resins, such as tetrafluoroethylene resin.

Matting agents can be used in the light-sensitive material and dye-fixing material. Examples of matting agents include the compounds described in Japanese Unexamined Patent Publication No. S61-88256, page 29, such as silicon dioxide, polyolefin and

polymethacrylate, and the compounds described in Japanese Patent Application No. 62-110064 and Japanese Patent Application No. S62-110065, such as benzoguanamine resin beads, polycarbonate resin beads and AS resin beads.

In addition, the layers constituting the light-sensitive material and the dye-fixing material can further contain a thermal solvent, a defoaming agent, an antibacterial/antifungal agent, colloidal silica and the like. Specific examples of such agents are described in Japanese Unexamined Patent Publication No. S61-88256, pages 26 to 32.

Image formation accelerators can be used in the light-sensitive material and/or the dye-fixing material. Image formation accelerators have the functions of accelerating the oxidation reduction reaction of the silver salt oxidizing agent and the reducing agent, accelerating the reaction of forming dyes from the dye-providing compounds, decomposing dyes, or releasing diffusible dyes, and accelerating the transfer of dyes from the light-sensitive layers to the dye-fixing layer. From the standpoint of physicochemical functions, the image formation accelerators are classified into compounds which have co-actions with bases/base precursors, nucleophilic compounds, high-boiling organic solvents (oils), thermal solvents, surfactants, and silver/silver ions. However, these substances generally have composite functions and usually have two or more of the above-

mentioned acceleration effects. Details of the substances are described in U.S. Patent. No. 4,678,739, columns 38 to 40.

Examples of the base precursors include a salt of a base and an organic acid causing decarboxylation by heat and compounds capable of releasing amines by an intramolecular nucleophilic substitution reaction, a Lossen rearrangement or a Beckmann rearrangement. Specific examples of the base precursors are described in U.S. Patent No. 4,511,493 and Japanese Unexamined Patent Publication No. S62-65038.

In the system which simultaneously carries out the heat development and the transfer of dyes in the presence of a small amount of water, it is preferred that the base and/or the base precursor are contained in the dye-fixing material in order to improve the storage properties of the light-sensitive material.

In addition, examples of compounds that can also be used as base precursors further include the combination of poorly water-soluble metal compounds and compounds (i.e., complex-forming compounds) capable of causing a complex-forming reaction with the metal ions forming the poorly water-soluble compounds as described in European Patent No. 210,660, and the compounds which form a base by electrolysis as described in Japanese Unexamined Patent Publication No. S61-232451. In particular, the former method is effective. It is effective that the poorly water-soluble metal compound and the complex-forming compound

are separately incorporated into the light-sensitive material and the dye-fixing material, respectively.

Various development terminators can be used in the light-sensitive material and/or the dye-fixing material according to the present invention in order to constantly obtain stable images against the variations of the processing temperature and the processing time on development.

The term "development terminator" as used herein refers to a compound which rapidly neutralizes a base or is reacted with a base after the appropriate development in order to reduce the concentration of the base in the layers, thereby terminating the development, or a compound which is capable of causing a co-action with silver and a silver salt in order to restrain the development.

/42

Specific examples of such development terminators include acid precursors which release an acid by heating, electrophilic compounds which cause a substitution reaction with a co-existing base by heating, nitrogen-containing heterocyclic compounds, mercapto compounds, and precursors thereof. Details of these compounds are described in Japanese Unexamined Patent Publication No. S62-253159, pages 31 to 32.

A substrate which withstands the processing temperature can be used as a substrate for the light-sensitive material and the

dye-fixing material in the present invention. Materials generally used are paper sheets and synthetic polymers (films). Specific examples of the materials include polyethylene terephthalate, polycarbonate, polyvinyl chloride, polystyrene, polypropylene, polyimide, celluloses (e.g., triacetyl cellulose), the materials obtained by incorporating a pigment, such as titanium oxide, into the above-mentioned films, synthetic paper sheets formed by polypropylene or the like, papers made of a mixture of a synthetic resin pulp, such as polyethylene, and a natural pulp, Yankee paper sheets, baryta-coated paper sheets, coated paper sheets (in particular, cast coating paper sheets), metal sheets, cloths and glass sheets.

These paper sheets can be used alone or as a coated paper, one surface or both surfaces of which are coated with a synthetic polymer, such as polyethylene.

Further, the substrates as described in Japanese Unexamined Patent Publication No. S62-253159, pages 29 to 31, can also be used.

The surface of the substrate can also be coated with a mixture of a hydrophilic binder and a semiconductive metal oxide, such as an alumina sol and tin oxide, and an antistatic agent, such as carbon black.

Examples of methods for imagewise exposing the light-sensitive material include a method wherein a scene, a person

and the like are directly photographed using a camera, a method wherein images are exposed through a reversal film or a negative film using a printer, an enlarger or the like, a method wherein original images are scanning-exposed through a slit or the like using an exposure device of a copying machine, a method wherein images are exposed to light emitted from a light emitting diode or various lasers through electric signals according to an image information, and a method wherein image information is output on an image display device, such as a CRT, a liquid crystal display, an electroluminescence display, a plasma display or the like in order to expose the displayed images directly to light or through an optical system.

Examples of light sources for recording images to the light-sensitive material include natural light, a tungsten lamp, a light emitting diode, a laser light source, and a CRT light source and the like as described in U.S. Patent. No. 4,500,626, column 56.

Further, the image-exposure can also be applied by using a wavelength conversion element which is composed of a combination of a non-linear optical material and a coherent light source, such as laser light. The term "non-linear optical material" as used herein refers to a material which is capable of generating a non linearity between the polarization and the electric field appearing on applying a strong photoelectric field, such as

laser light; preferred examples of such materials include inorganic compounds, typified by lithium niobate, potassium dihydrogenphosphate (KDP), lithium iodate and BaB_2O_4 , urea derivatives, nitroaniline derivatives, nitropyridine-N-oxide derivatives, such as 3-methyl-4-nitropyridine-N-oxide (POM), and the compounds described in Japanese Unexamined Patent Publication No. S61-53462 and Japanese Unexamined Patent Publication No. S62-210432. Known examples of the form of wavelength conversion element include a single crystal light waveguide form and a fiber form, and any of these can be effectively used.

Examples of the image signals that for the above-mentioned information include an image signal obtained from a video camera, electron still camera or the like, a television signal, typified by Nippon Television Signal Code (NTSC), an image signal obtained by dividing an original into many dots by using a scanner or the like, and an image signal made by using a computer, typified by CG and CAD.

The light-sensitive material and/or the dye-fixing material can be in the form having a conductive exothermic layer as a heating means for the development of heat or the diffusion transfer of dyes. In this case, the transparent or opaque exothermic elements described in Japanese Unexamined Patent

Publication No. S61-145544 can be used. The conductive layer also functions as an antistatic layer.

The heating temperature in the heat development step is from approximately 50 degrees Celsius to approximately 25 [sic] degrees Celsius but, in particular, a temperature range of from preferably approximately 80 degrees Celsius to approximately 180 degrees Celsius is effective.

/43

The diffusion transfer step for dyes can be carried out simultaneously with the heat development, or can also be carried out on completion of the heat development step. In the latter case, the heating temperature in the transfer step can be in the range of from room temperature to a temperature in the heat development step, but the heating temperature is preferably in the range of from approximately 50 degrees Celsius to a temperature 10 degrees Celsius lower than the temperature in the heat development step.

The transfer of dyes can occur by heat only, but a solvent can be used in order to accelerate the transfer of dyes.

Further, as described in detail in Japanese Unexamined Patent Publication No. S59-218443 and Japanese Unexamined Patent Publication No. S61-238056, a method of heating in the presence of a small amount of a solvent (in particular, water) to carry out the development and the transfer of dyes simultaneously or

in succession can be effectively applied in the present invention. In this method, the heating temperature is preferably in a range of from 50 degrees Celsius or more to the boiling point of the solvent or less. For example, when the solvent is water, the heating temperature is preferably from 50 degrees Celsius or less to 100 degrees Celsius or less.

Examples of solvent which can be used to accelerate the development and/or the transfer of diffusible dyes to the dye-fixing layer include water and basic aqueous solutions of an inorganic alkali metal salt or an organic base (examples of the base include those described above on the image formation accelerators). Examples of solvents further include a low-boiling solvent and a mixture of a low-boiling solvent and water or the basic aqueous solution can be used. Further, the solvent can contain surfactants, antifoggants, poorly water-soluble metal salts, complex-forming compounds and the like.

These solvents can be used by adding them to the dye-fixing material and/or the light-sensitive material. The amount of the solvent used can be a small amount which is smaller than the weight of the solvent corresponding to the maximum swelled volume of the total coated layers (in particular, smaller than the amount obtained by subtracting the weight of the total coated layers from the weight of the solvent corresponding to the maximum swelled volume of the total coated layers).

Examples of application methods of a solvent to the light-sensitive layer or the dye-fixing layer include the method described in Japanese Unexamined Patent Publication No. S61-147244, page 26. Further, the solvent can be incorporated in advance in the light-sensitive material and/or the dye-fixing material, for example, by encapsulating the solvent in microcapsules.

In order to accelerate the dye transfer, a system which incorporates a hydrophilic thermal solvent, which is in the form of a solid at room temperature but is melted at a high temperature, into the light-sensitive material or the dye-fixing material can be employed. The hydrophilic thermal solvent can be present in either the light-sensitive material or the dye-fixing material or in both materials. The hydrophilic thermal solvent can be incorporated into any of an emulsion layer, an intermediate layer, a protective layer and a dye-fixing layer, but the incorporation into the dye-fixing layer and/or a layer adjacent to the dye-fixing layer are particularly preferred.

Examples of the hydrophilic thermal solvent include ureas, pyridines, amides, sulfonamides, imides, alcohols, oximes, and heterocyclics.

Further, in order to accelerate the dye transfer, a high-boiling organic solvent can be incorporated into the light-sensitive material and/or the dye-fixing material.

Examples of heating methods in the heat development step and/or the dye transfer step include a method wherein there is contact with a heated block or plate, a method wherein there is contact with a hot plate, a hot presser, a heat roller, a halogen lamp heater, an infrared or far infrared lamp heater or the like, and a method involving passing through a high-temperature atmosphere.

In the case of superposing the dye-fixing material onto the light-sensitive material and applying a pressure to the assembly for the purpose of closely superposing them, the pressing method and the pressing conditions as described in [page 43 END]